Proceedings of the

1968 TECHNICAL SESSION

ON

CANE SUGAR

REFINING RESEARCH

San Francisco
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OPENING SESSION

The 1968 Technical Session on Cane Sugar Refining Research was called to order by Henry Gerstner, past President of the Cane Sugar Refining Research Project and General Manager, Colonial Sugars, Gramercy, Louisiana. Mr. Gerstner then introduced T. M. Rinehart, Atlas Chemical Industries, who was the Chairman of the morning technical session.

FIRST SESSION: Tom Rinehart, Atlas Chemical Industries, Chairman

REGENERATION OF ADSORBENTS; BONE CHAR AND SYNTHAD

George W. Muller
Kerr-McGee Chemical Corp., Philadelphia, Pa.

When the sugar refineries supported the Bone Char Project at the National Bureau of Standards they stood alone. Today there is a renewed interest in the fundamentals of calcium phosphates, whether they be in bone, teeth, fertilizer, or bone char. There was a symposium last year in France on calcium phosphates. This year two meetings were held: a Gordon Research Conference and a meeting at Princeton, where discussion was primarily on research in progress. Earlier this month in Washington, I attended a large meeting of European and American investigators who covered a wide range of subjects pertaining to calcium phosphates. The symposium papers demonstrated a wide interest in hydroxyapatite, whether its use was for a laser, fluorescent light, biological materials, teeth, or bone. The chemist, the physicist, the mineralogist, the biologist, the dentist, the doctor have all awakened to the age old substance, calcium phosphate.

Bone char is the major refining agent for the cane sugar industry. Regeneration of bone char and Synthad is concerned with maintaining peak activity.

Bone char, activated granular carbons and ion exchange resins all require control of liquor temperature, density and pH. Brilliant liquor is required for top efficiency of decolorizing adsorbents.

Bone char and Synthad are adsorbents with a broad spectrum of activity which overlap both granular carbons and resins.

Bone char has maintained its lead in sugar refining for several reasons: its long life, its hardness, and its pH buffering quality. It is also foremost because it was the first installed. The inertia of huge char houses maintains the status quo.

New adsorbents come into the refineries with new techniques and enthusiasm. Char is seldom evaluated in new equipment save as in American Sugar's CAP system(1), and years ago at Refined Syrups in the Herreschoff kiln. (2)

Both the CAP system and the Herreschoff have been modified for the granular carbons. The ion exchange systems have shown continuing progress in their efficient use in new techniques and equipment.

The refiners tend to allow the char house to run by itself. The huge bulk of char and liquor in process can hide operating mistakes in affining, clarification, and remelt recovery.

The increase in daily melt has forced most refiners to simplify their char liquor system. Carbonatation and phosphate defecation have been installed in many refineries to remove one-third or more of the color load and some of the ash. The non-sugars are generally sent through the remelt system.

(1) Marcy, W., S. I. T. 20, 76(1961)
(2) Gillette, E. D., S. I. T. (1948)

Today more liquor passes over the char cisterns, but the total non-sugar load to char is less in most refineries.

Regeneration of the char today is still rule of thumb. The char is washed by hot or warm water for 10 to 20 hours at about 300 cu. ft. per hour. The char is generally purged of adhering water by the air drying cycle. The kiln temperatures are satisfactory from over 900° F. to 1050° F. (480° C. to 560° C.).

New char injection, which is a step in regeneration, is also rule of thumb.

Generally enough new char is used to replace the dust formed and the grain discarded. Repairs of char kilns require temporary decrease in the total stock - so new char injection lags during the late fall and winter months. The quality of the char may follow the erratic injection rate.

Systems using the hearth furnace should be less erratic in char injection.

Sometimes an economic squeeze dictates a lower injection rate. The slow change in char decolorizing ability is scarcely noticed. But in a later year the whole char quality seems to have gone down.

The 1930's was a time of experimentation on plant scale throughout the world.

During this period, the air gravity separator, embodied in the Sutton, Steele & Steele, or Kipp Kelly became a prime piece of equipment for improving the quality of the char.

Battery system of sweetening off and washing became standard in some refineries.

The work of Drs. Victor Deitz, Frank Carpenter, and others in the 1950's at the Bureau of Standards now seems neglected. The enthusiasms aroused by the Bone Char Conferences have faded.

But where are we now? In some refineries the SS&S has been neglected.

An air gravity separator should be installed and working on each char. Or at the very least - in a three or four char system refinery - the best grades should have access to the SS&S and a portion of the best grade chars should pass over it several times a year.

The granular carbons and ion exchange resins have no equivalent device to remove individual blocked useless particles. The carbons are burned to restore the underlying fresh surface. The fines, and the soluble ash formed from combustion of the organic matter are discarded in the slurry water.

The ion exchange materials used for color removal are very sensitive to soluble ash. Eventually the bed of resin is exhausted and is discarded in bulk.

In a broad sense, regeneration of bone char covers more than the washing and burning cycles. Regeneration of char and Synthad also includes: injection of new material, removal of dust, removal of heavy exhausted char particles, and drying of char.

The treatment of char in the settling and liquor cycles affects the regeneration. The static bed of char, after washing, sends grains to the kiln which have been differently treated. The counter current CAP system approaches the ideal that all the char granules are treated the same - so the regeneration can be more efficient.

Granular carbons, presenting new surface to the liquors, generally are little affected by previous cycles.

Bone char, and to some degree the resins, carry the history of previous liquor and regeneration cycles into the new cycle. This complex history that can modify the char activity is seldom taken into account.

Heavy non-sugar loads should be followed by a longer washing, possibly a slower kiln draw rate. Bacterial growth, as revealed by turbid sweet waters, char waste waters, and draining waters, certainly will block pores with gummy polysaccharides. Sulphide forming thermophiles may leave enough sulphide to darken the lead acetate test in the lye test and lead to erroneous conclusion of overburning.

Highly active char - such as new char that has been washed and then loaded with non-sugars - may catch on fire on passing through the dryer and lose some of its hard bought carbon rapidly. The underburning of char, resulting in carbon-blocked pores, particularly affects many following cycles. Overburning, resulting in lower surface area, loss of fine pores, and increased size of crystallites, may never be overcome.

The attitude that the char house takes care of itself is a sure sign that the quality will go down hill!

Physical qualities that are characteristic of good service chars are: fairly uniform screen size, high surface area, high pore volume, low bulk density, and the particle density about the same as new char. Service bone char and Synthad should be reasonably hard, to resist breakdown throughout a long life.

Chemical characteristics may be listed: high pH and strong buffering capacity over the whole liquor cycle and sweet water cycle is a prime consideration. The carbon content should be that of new char or somewhat less. High carbon content indicates poor regeneration over many cycles. High sulphate can be remedied by better washing. High sulphide may indicate local high temperature overburning. Dark lye tests indicate excessive organic matter still on the regenerated char. A high DH (3) on freshly kilned char indicates low temperature regeneration.

The chemical-physical tests, using two organic adsorbents CTAB and OT, devised by Dr. Abram and Dr. Bennett of Tate & Lyle (4), bring us more information on the activity of the char surface.

During the last year the Kerr-McGee laboratory at Philadelphia has determined the physical characteristics of chars from many refineries. As usual, no single parameter classifies the char. In some cases refinery personnel classified the chars as good or poor in refining quality. The mercury porosimeter (5) was used to determine pore size, pore distribution, and pore volume.

Table 1 shows the pressure required to force mercury into pores of various radii.

Table 1

Pressures required for mercury intrusion	
Pressure-PSI	Pore size-Å Radii
10,000	106
20,000	53
30,000	35
50,000	21
Pore volume by desorption	
N_2 desorption	125-20 Å
H_2O desorption	125-2.5 Å
He desorption	To the finest pores
Size comparison	
325 Mesh opening = 4,400 Å	
1.0 Micron = 1.0×10^4 Å	

The upper limit of 60,000 p. s. i. includes pores down to about 10 Angstrom units. It happens that most of the pore volume of the char lies within the range of the mercury porosimeter. The surface area as determined by nitrogen at liquid nitrogen temperatures is that made available by this same range of pore sizes. There is no unused pore volume or surface area for decolorizing purposes in bone char and Synthad. The gas

(3) Guerin, J., Proc. Tech. Sess Bone Char 1959, p121 (1960
(4) Abram, J. C., and Bennett, M. C., J. Coll. and Interface Sci. 23, 513 (1967); 27, 1 (1968)
(5) Manufactured by American Instrument Co., Silver Spring, Md. and others.

carbons with most of the pore volume and area in the micropore region are poor decolorizing carbons, as the large color molecules can't enter the extreme micropores. Several of the tables and charts are modifications of those in the Atlas Chemical Company brochure "A Symposium on Activated Carbon".

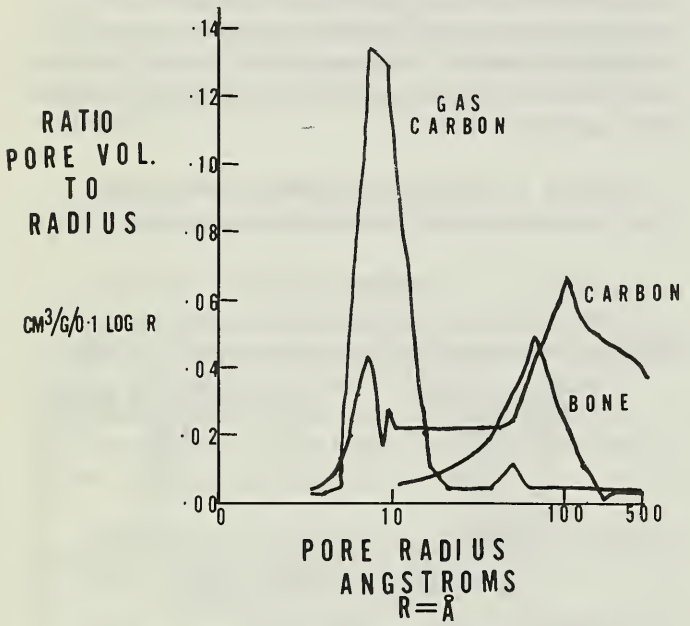

Chart 1 Pore volume distribution in a gas carbon, a decolorizing carbon, and new bone char.

Chart 1 shows the relationship of pore distribution of a gas carbon, a granular decolorizing carbon and a new bone char. The actual pore volume in new char is not large. The refiner should take care to maintain his service char pore volume by all means! Once lost, it is seldom recovered.

Bone char and the decolorizing granular carbons both have pores in the "transitional" pore range 20Å to 1000Å radius. The micropores of gas carbons do not decolorize sugar solutions.

Chart 2 sketches the size of very small particles on the same logarithmic scale that is used to illustrate the pore size distribution. The red blood cell is easily seen by the optical microscope. Virus particles, bone crystallites, and some large molecules are easily in the range of the electron microscope.

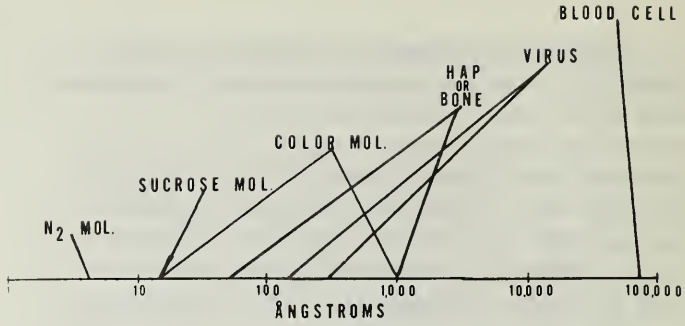

Chart 2 Size relationship of small particles. The electron microscope range may extend from optical to about 20 Angstrom radius. Note scale is logarithmic.

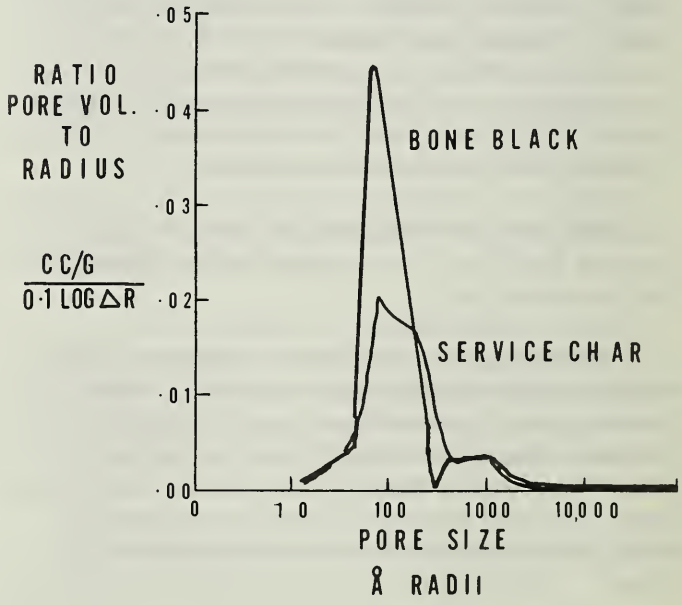

Chart 3 Pore distribution of a new char and a typical average service char.

Chart 3 illustrates the pore volume distribution of new bone black and an average service char.

Chart 4 shows the cumulative intrusion of mercury at increasing pressures to obtain the final pore volume. New chars have almost 0.3 cc. pore volume per gram of char. A dense old char may have as little as 0.1 cc.

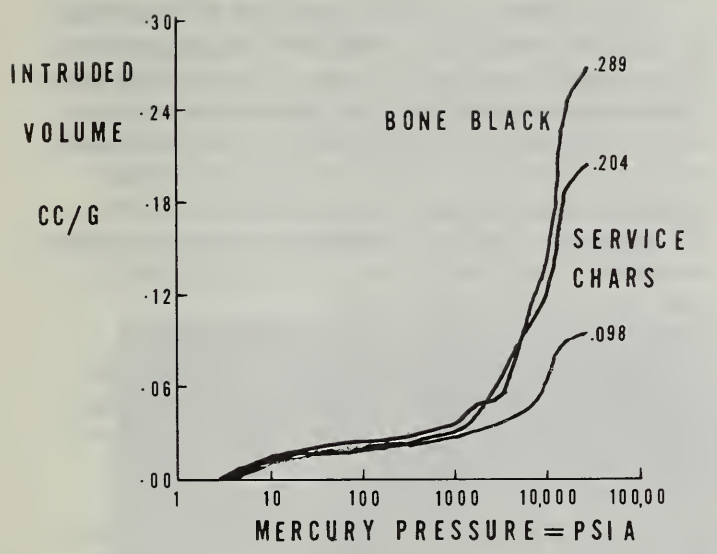

Chart 4 Cumulative intrusion by mercury into char pores of new bone black and service chars.

Table 2 lists physical characteristics desirable in good service char. The limits may be broader. No one parameter determines the rating of the char. Low surface area may be offset by open porosity and strongly active adsorption sites. I have used observations of refinery personnel as to where the char quality lay in multiple system char houses.

Particle density of new char and the good char should be the same. Some old service chars, loaded with carbon, had lower densities, due possibly to blocked empty pores. Other hard old chars seemed to be heavily mineralized and the particle density approached the specific gravity of the mineral hydroxyapatite. These particles were probably in the refinery for longer than the average, as calculated by new char injection.

The standards of regeneration have been studied in detail by the Bone Char Research Project. A most important result of the NBS regeneration tests was the need to burn off adsorbed organic matter at 250-300° C. That is a zone of low temperature and moderate oxygen content is required. This destruction of organics leads to better pH liquors from the char. But, what refinery has designed new hearth kilns to take advantage of these findings by Dr. Carpenter? Refineries have generally set kiln temperatures and draw rates to obtain the satisfactory pH and lye tests.

New char is injected to maintain volume. The removal of old char by the SS&S is more erratic, but it is the most neglected means of maintaining high quality char.

The washing of char should be further studied and more thoroughly controlled. Water lines supplying the char filters may be partly blocked, so the low volume of water tends to expose the char surface and channel.

Refineries should study the feasibility of backwashing cisterns. Refined Syrups has done an able job on this matter. Back wash rates may be higher than the normal down wash of cisterns, and thus the cycle time may be reduced.

Table 2. --Physical characteristics of bone chars

Parameter	New	Good	Poor
Hardness NBS %Breakdown	18-29	10-15	<5
%Dust	9-14	8-11	<5
Bulk Density, lb/ft^3	40	52-57	>70
Particle Density, g/cc	2.7	2.7	<2.7 or >3.0
Pore Volume, cc/g	0.29	0.27	<0.17
B. E. T. Surface Area, m^2/g	120	70	<40

The impurities of the heavily loaded top layer of char in the backwashed cistern are sent directly to the sewer.

The use of warm water vs. hot water for washing char needs reviewing. Hot water still removes sulphate, but may remove more reversibly held organic matter than does warm water. The risk of fermentation during cold water wash or air drying of warm char is too great. Polysaccharides formed have made char sticky. Refineries having narrow louvred char driers over Herreschoff kilns have to follow warm water with hot to eliminate stickiness. New char washed with cool water is not sticky - it runs easily through driers.

Most refineries have tubular exchangers to recover the heat from the hot water char washings.

To sum it all up, proper regeneration of char requires clean liquor and water. New char injection rates should be high enough to maintain the required decolorization. The air gravity separator should be used and maintained in working order. Kilns and driers should be clean and free of fly ash accumulation. Burned out retorts should be replaced as soon as practical. New technical and operating supervisors should have access to, and use of, the many excellent reports and conferences of the Bone Char Project.

As the recent scientific meetings on hydroxyapatite show - we know a great deal about bone, but there is far more to learn.

DISCUSSION

M. C. Bennett (Tate and Lyle, correspondence): We have made a series of electron microscope slides, showing bone as a natural material and then carbonized bone, new bone char, service chars, and finally the carbon component in new and service chars. The key to obtaining these pictures was the preparation of ultra microtome sections, about 400Å in thickness.

To obtain ultra thin sections of material it is first necessary to embed the specimen in a plastic medium. It was known from previous experience that the embedding of porous specimens can be spoilt by the inclusion of pockets of gas which are trapped by the viscous unpolymerised embedding medium. If, however, the embedding medium is poured over the specimen in vacuo, this difficulty can largely be overcome.

Vacuum embedding was carried out on the specimens using Araldite, Methacrylate, Epikote, and N. H. P. Metallurgical Mounting Plastic as the media.

It was evident that the methacrylate reacted with the bone char since discoloured blocks were obtained which were only partially polymerised. The use of methacrylate containing a greater percentage of catalyst was tried. Although the resulting blocks polymerised, the material contained in them collapsed. The N. H. P. was too viscous and quick setting to give adequate penetration of the specimens and the Araldite and Epikote media did not polymerise, presumably because the specimen had an inhibiting effect. In an attempt to overcome these difficulties the bone chars were soaked in a 1% solution of Bedacryl in benzene. The Bedacryl was allowed to set for 1 hour at room temperature followed by heating for two hours at 30° C. In this way it was hoped to 'mask off' the char and prevent any inhibiting action it might have on the polymerisation process of the mounting medium. The methacrylate blocks would still not completely set, the araldite blocks were too soft for sectioning, but the Epikote preparations were of a suitable hardness and were subsequently used to obtain the sections examined for this report. The composition of the Epikote resin used was a 4:1 mixture of Epikote Resin 816 and 'Epikure' t.

Sectioning

The blocks obtained for each specimen were trimmed to a pyramidal form, the tip of which contained the char particles. This block was then set up in the ultra-microtome which was fitted with a diamond knife. The bath behind the

knife edge was filled with distilled water and the sections floated on this as they were cut. The sectioning of the blocks was difficult, the embedding medium not having completely penetrated the material and all but the thinnest sections crumpled and shattered at the knife edge.

The sections were placed on carbon coated copper specimen support grids for examination in the electron microscope.

Microscopy

Photomicrographs were prepared using a Siemens Elmiskop 1 electron microscope working at an accelerating voltage of 100 KV. The photomicrographs have been prepared at 100,000 x magnification, and the photos carry a scale

Figure 1. Section of a bone particle. The appearance is similar to that of sections made on a number of different types of bone particles selected from a sample of crushed, sieved bone supplied by British Charcoals and Macdonalds Ltd. This is the material from which bone charcoal is manufactured.

Two types of calcium phosphate particle can be distinguished: acicular (30 - 50 Å wide and 700 - 800 Å long) and plate-like (400 Å diameter). The latter lie in rows with a separation of about 200 Å and in electron-micrographs at lower magnification (not shown here) the striations formed by this regular array can be seen to have a periodicity of 660 Å. This periodicity in the mineralization of collagen during bone formation has been demonstrated by Mjor (1) and by Dudley and Shapiro (2).

(1) Anat. Record 144, 327, (1963)
(2) J. Biophys. Biochem. Cytology 11, 627, (1961)

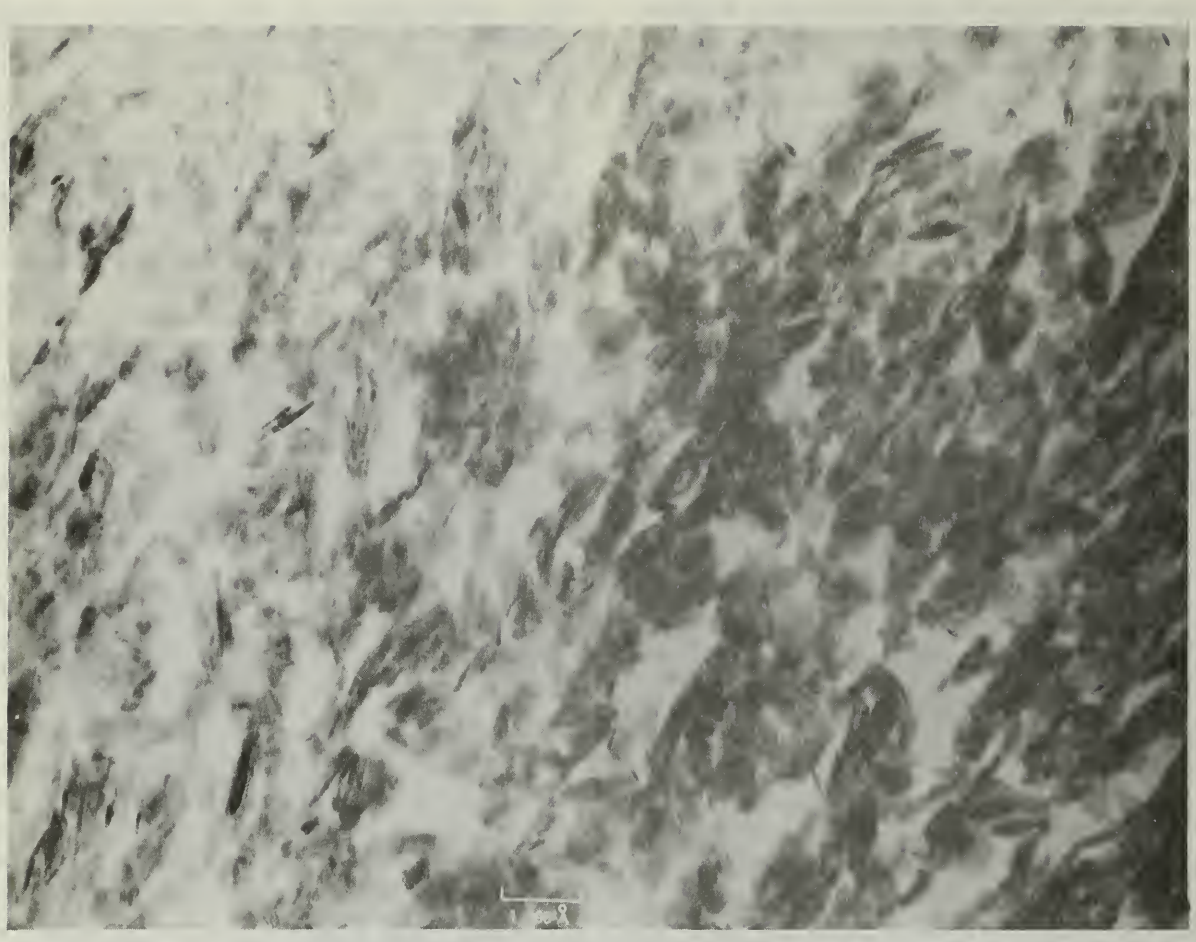

Figure 2. Section of bone hydroxyapatite. Bone particles as used in Fig. 1 were freed from organic material by refluxing in ethylenediamine for 24 h. followed by prolonged water washing (3). After this treatment the apparent carbon content of the sample was 0.6%.

The sample shown in Fig. 2 had been heated at 350° C. for 3 h. and its BET (N_2) surface area was 135 m^2/g. The acicular particles are shorter and wider than in the original bone and the plate-like particles slightly larger in diameter. The growth of the phosphate crystallites on heating has been followed in detail in these laboratories. On prolonged heating the fine structure disappears completely to be replaced by a coarsely sintered structure.

(3) Beebe et al. J. Phys. Chem. 64, 1300, (1960)

Figure 3. Sample of unused new bone char washed with distilled water for 24 h. and subsequently kilned at 500° C. for 1 h. Its surface area was 106 m^2/g. It is not possible to distinguish the carbon component in this micrograph; the carbon phase can be demonstrated by the technique described for figures 8 and 9.

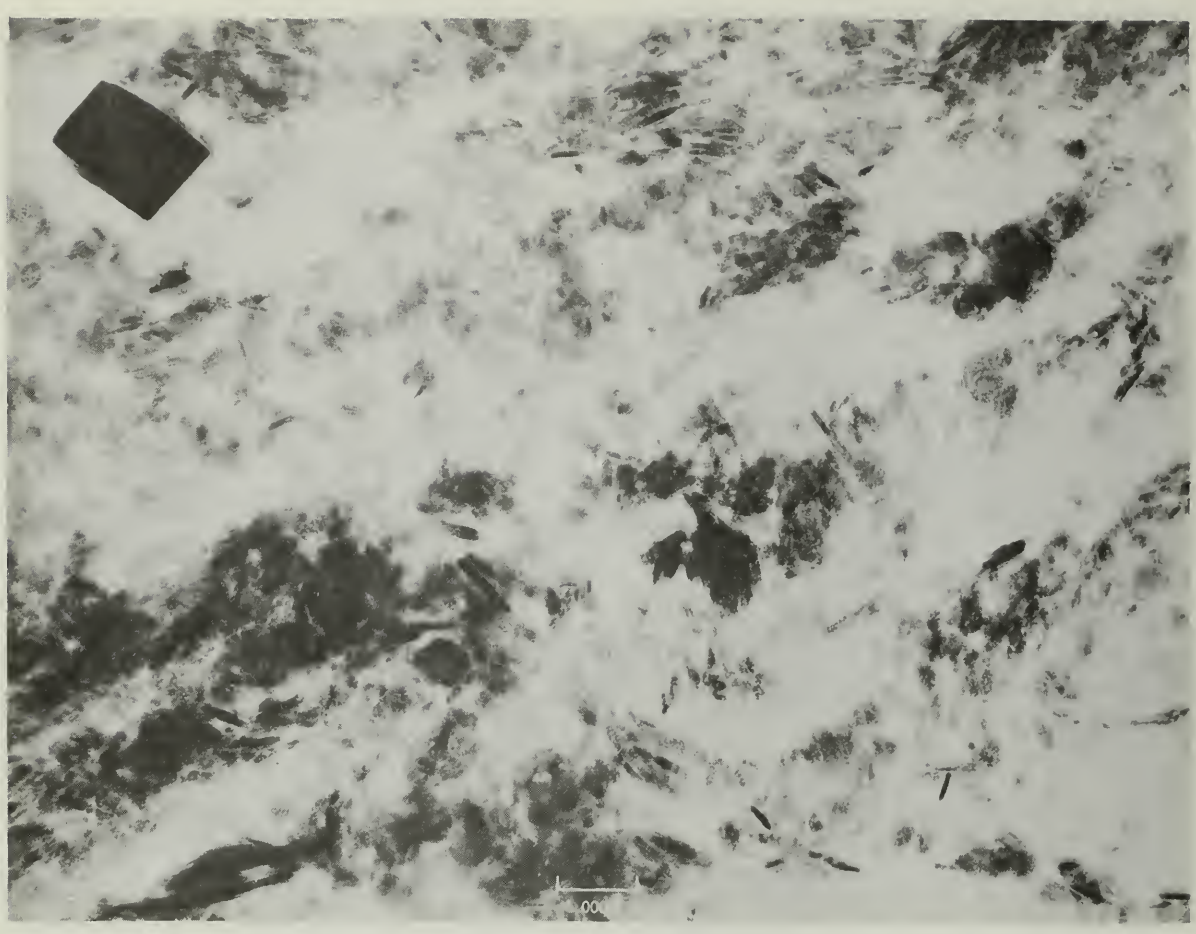

Figure 4. Sample of new Synthad, with a structure similar to that of new bone char. The large electron-dense block of material is probably a non-phosphate mineral particle, possibly from the clay that is used as a binder in Synthad.

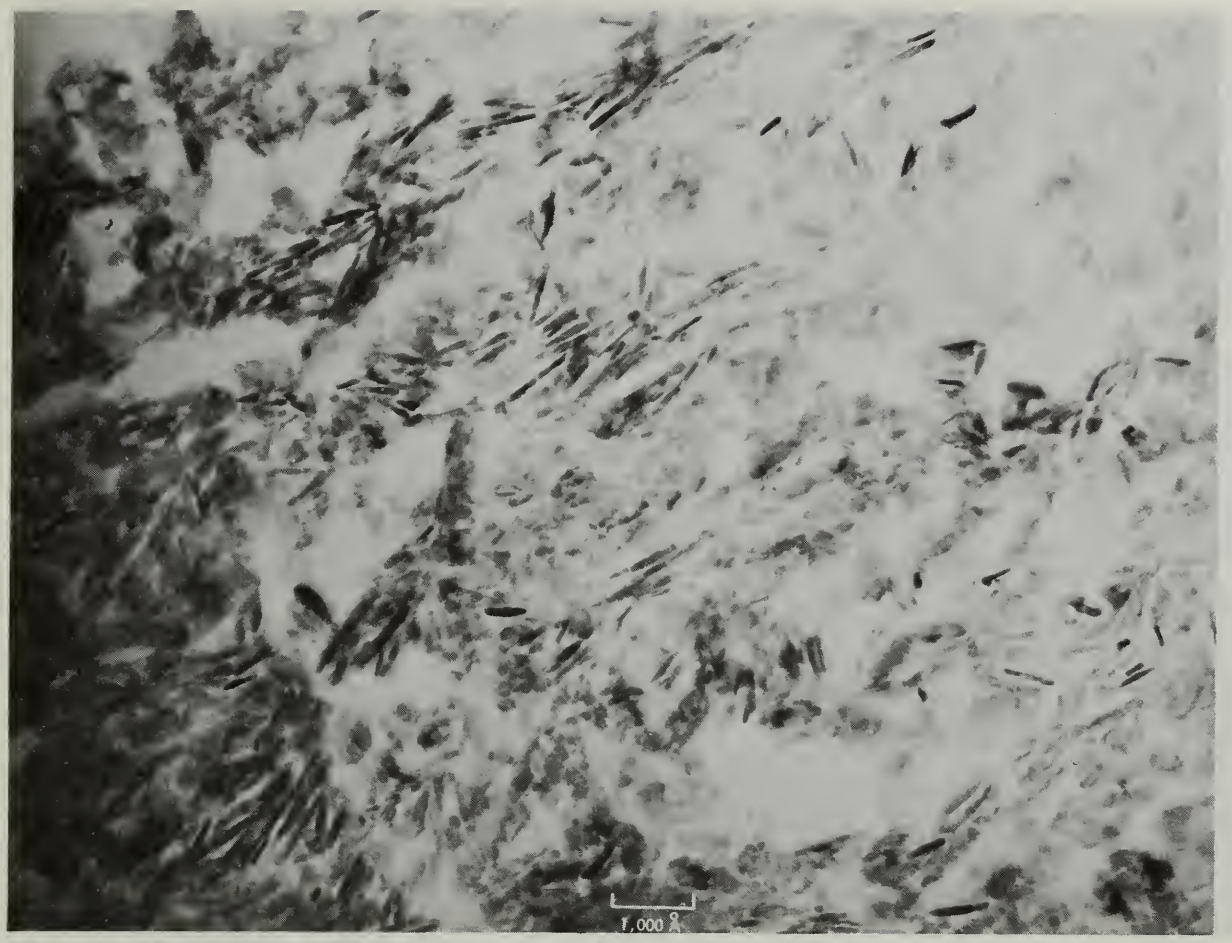

Figure 5. High quality stock char with a surface area of 85 m^2/g. The acicular particles are only slightly larger in diameter (ca. 100 Å) than those of unused new char.

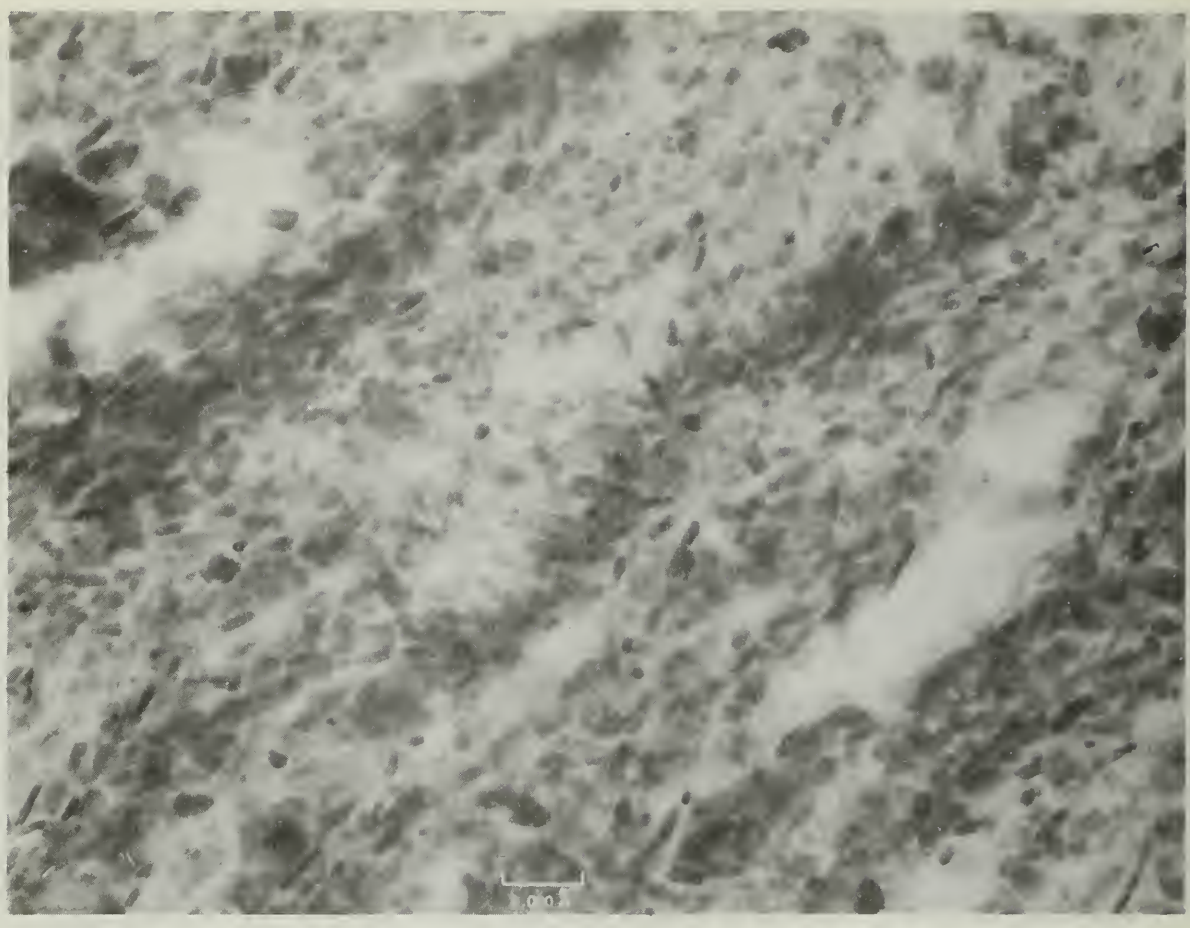

Figure 6. Sample of low quality stock bone char which has a surface area of 52 m^2/g. The acicular structure has almost disappeared but because of the high carbon content (11. 1%), there has been little sintering and subsequent growth of the coarse structure. It is also possible that CO_2 has entered into the hydroxyapatite lattice and changed the structure from a columnar to a tabular type.

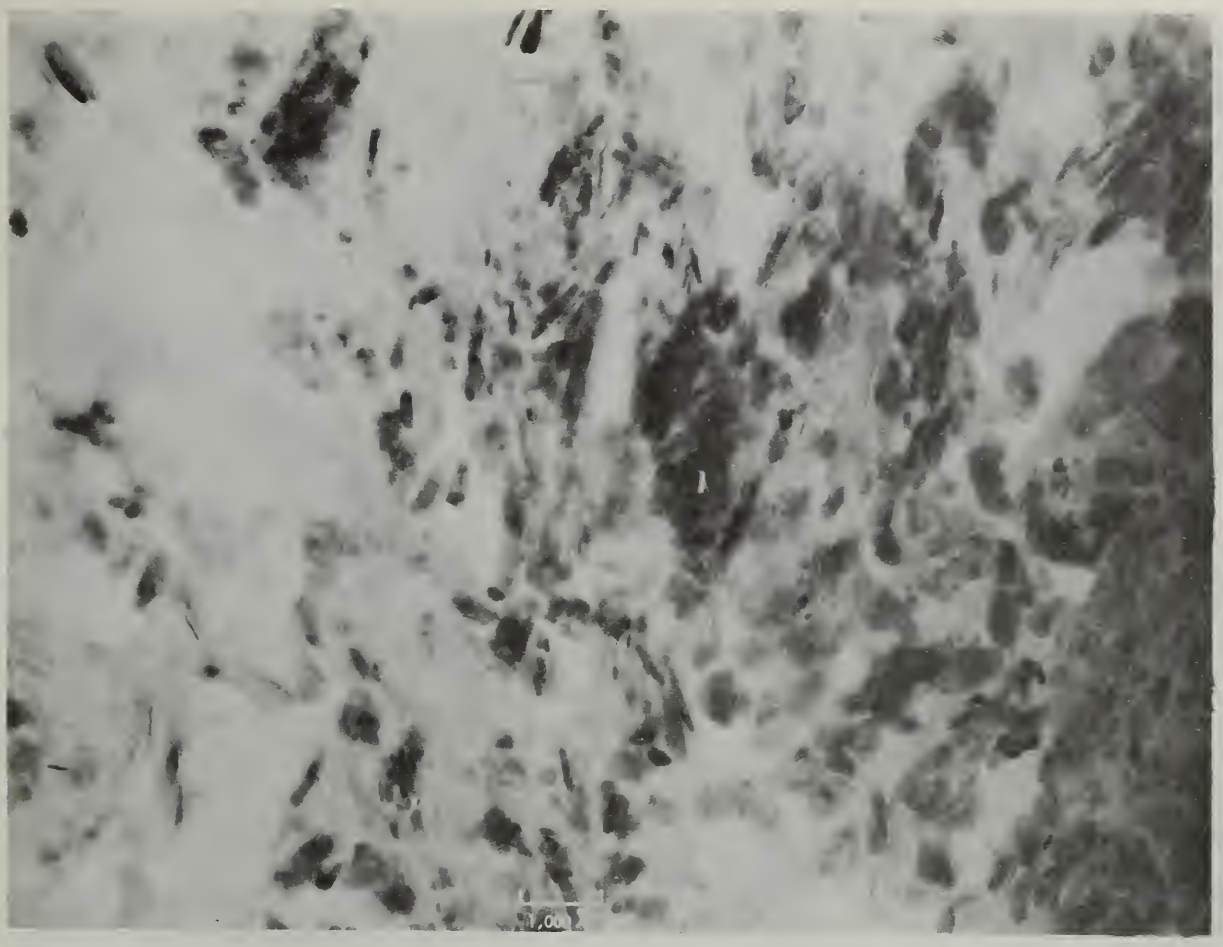

Figure 7. Sample of low quality stock bone char with a surface area of 40 m^2/g. It has a very low carbon content (4.3%) and sintering has proceeded with a marked increase in particle size of the coarse structure.

Figures 8 and 9 show the different dispersity of carbon in stock and new chars. For these electron micrographs, sections were cut from blocks containing a stock char (7.6% carbon, carbon surface area ca. 500 m^2/g. carbon), and a new char (7.1% carbon, carbon surface area ca. 1000 m^2/g. carbon). The sections were picked up on carbon-coated palladium grids and these were then floated upside down on 6 N HCl for 4 h. The grids were removed and washed free from acid for examination in the electron microscope.

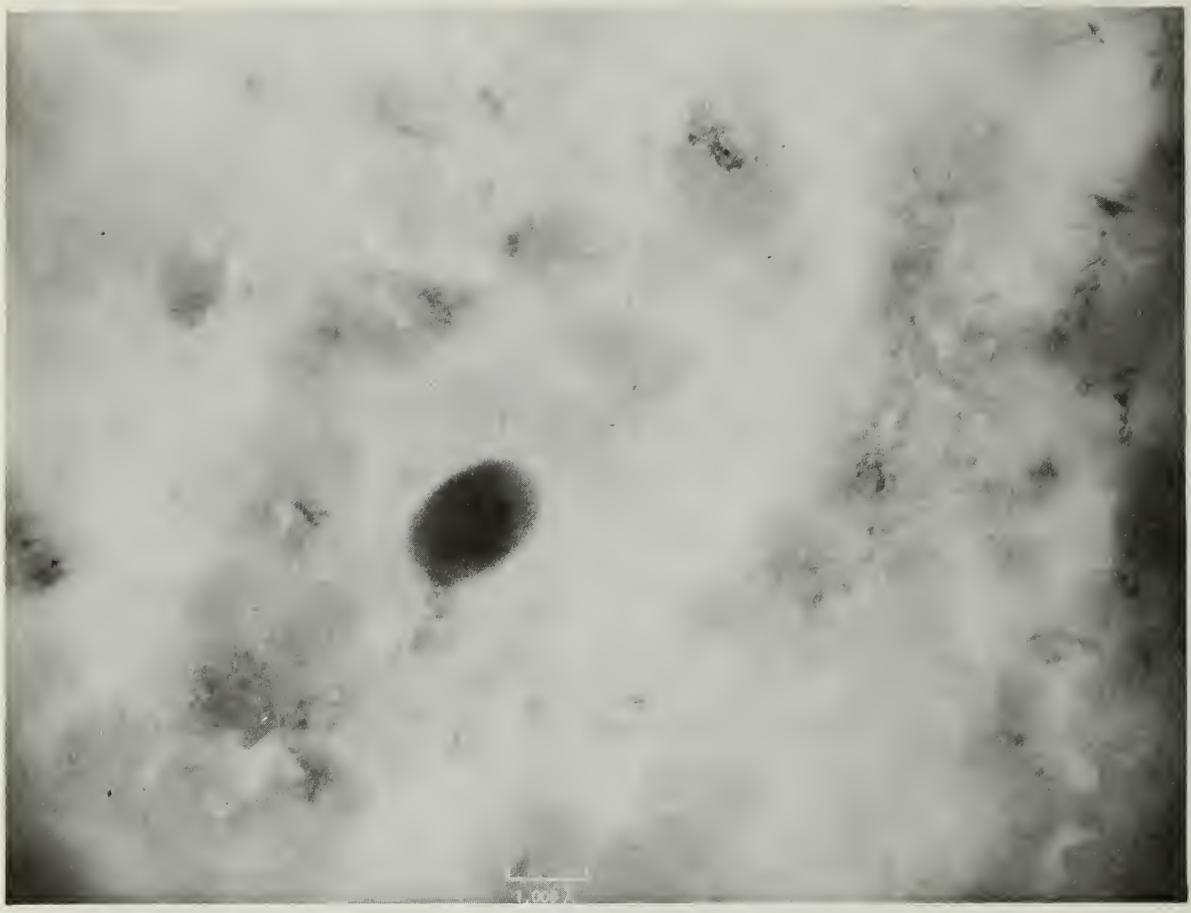

Figure 8. Carbon in stock char. Clear evidence is seen of accumulated carbon deposits as cylinders ca. 100 Å in diameter. These perhaps reveal the shape of pore in which carbon had been deposited or the shape of the hydroxyapatite crystallite covered by it.

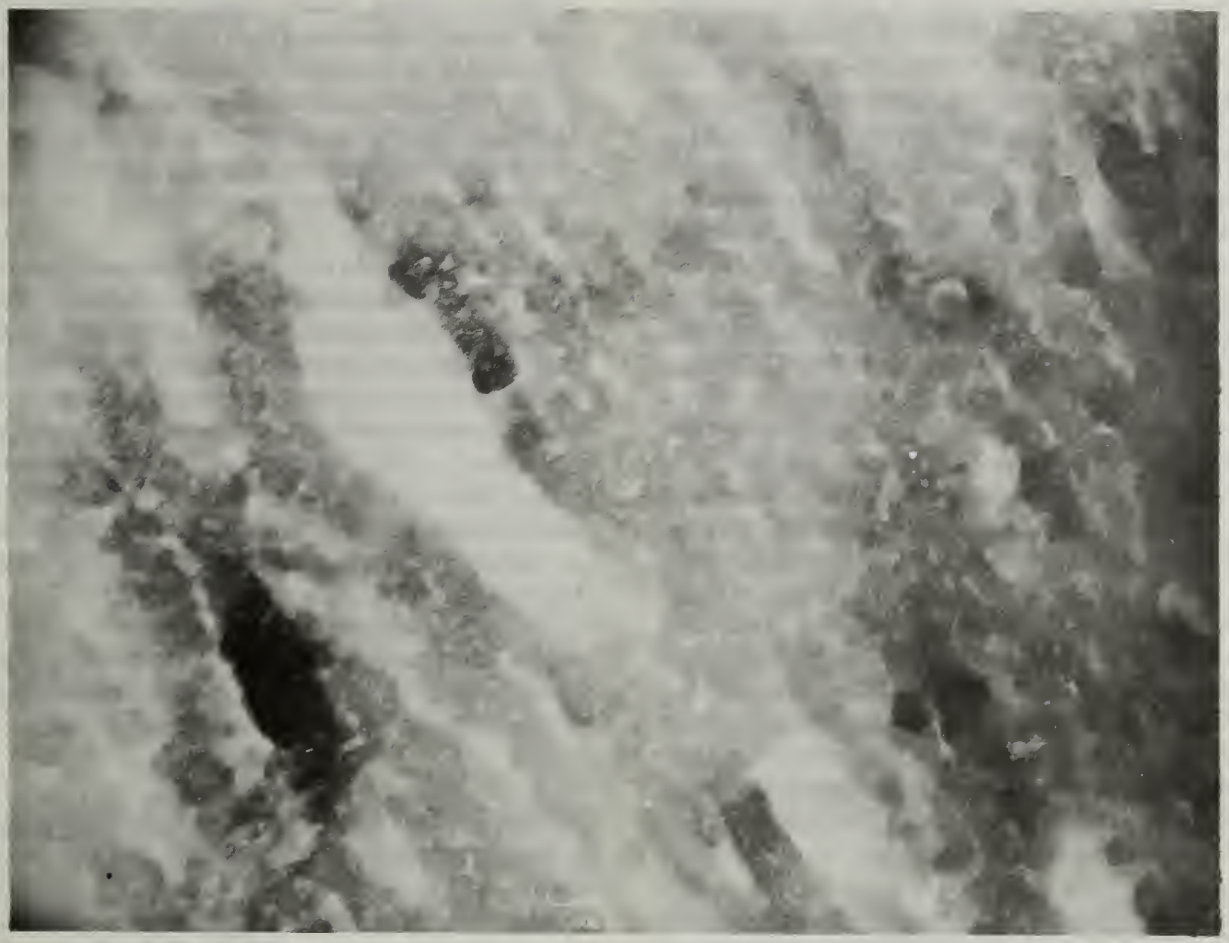

Figure 9. Carbon in new char. It is not possible to distinguish any carbon deposits, perhaps because the carbon is dispersed too finely to produce adequate contrast in the electron microscope.

Acknowledgement

The experimental work was carried out on behalf of Tate and Lyle Research Centre by Aeon Laboratories, Beech Hill, Ridgemead Rd., Englefield Green, Egham, Surrey.

R. S. Joyce (Pittsburgh): I wonder if you would care to comment on the ability of the carbon to accumulate on its surface a layer of iron complex that is not accumulated by Bone Char. What can you say about the mechanism of this reaction?

G. W. Muller (Kerr-McGee): The adsorption of an iron non-polar complex on granular carbon could also occur on the carbon of bone char. Granular carbons could adsorb an organically complexed calcium or other metal.

R. S. Joyce: You mentioned that adsorption correlated with fine pores to a minimum of 2.5 Å. How did you calculate this?

G. W. Muller: I obtained these from Tom Rinehart's tables (1). Water vapor can be used for measuring pore size down to two and one-half angstroms.

H. Van Diermen (Pepsico): I should like to ask a question about your total area test. You mentioned the use of OT and CTAB. These tests are quite complicated and not easy to do. What do you consider the most useful test for the total area of bone char in daily operation?

G. W. Muller: The area as you would determine it by nitrogen adsorption is a lengthy

(1) A Symposium on Activated Carbon, Atlas Chemical Industries, (1968)

test for a physical chemist to make in the laboratory. But the CTAB-which means Cetyl Trimethyl Ammonium Bromide-is a material that is adsorbed on the carbon surface of a complex bone char hydroxyapatite material. The OT of Dr. Abram and Dr. Bennett is dioctylsodiumsulfosuccinate. In water that material is adsorbed both on the hydroxyapatite structure and on the carbon, while in a benzene solution, OT is adsorbed only on the hydroxyapatite. So you can measure the surface of only the carbon, or only the hydroxyapatite, or the surface of both of them, which is approximately the surface by nitrogen adsorption. These tests are being run by research laboratories of some of the refineries for the purpose of checking the findings of Drs. Bennett and Abram.

As to its practical applicability, I don't believe you would make it daily, but rather every three months to check the surface. I understand that the Tate and Lyle R and D laboratory is now using this method to grade bone char, rather than a column test method, which is even more tedious. This method is more rapid than the column test.

J. F. Dowling (Refined Syrups): One of the things to come out of the Bone Char Research Project was the addition of divalent cation to the feed liquor(1). At that time they stated you could get better decolorization if you had more calcium in the clarified liquor going to char. Since that time I haven't heard of any refineries adding calcium to their feed liquor before decolorizing. I wonder if you would care to make a statement whether this is good, bad, or indifferent or is anybody doing it?

G. W. Muller: I have no practical experience with it.

F. G. Carpenter (SRRL): I can say that a few of the refiners are in fact using that method. It isn't so much a case of adding calcium as it is making sure that you have as much calcium as you have polyvalent anions. This way you have at least as many divalent cations as you have divalent anions. Many liquors already achieve that balance, but once in a while you find some that don't. With these, the improvement in color removal can be spectacular. In several refineries they do, in fact, check the EPA, and when the balance is out, they add the necessary calcium.

J. F. Dowling: In connection with adding the calcium, one of the things that we found was that the calcium in the water extract of the char was directly related to the calcium in the feed liquor, so once you start adding calcium to the feed liquor you will find that you are going to have more calcium in your char liquor because you are not going to burn it all in during the regeneration cycle. You could presumably get around this by increasing the wash water, but again the economics begins to come into it.

F. G. Carpenter: You can cut down in that calcium in the first liquor off char by using a slightly higher reburning temperature.

J. F. Dowling: We went as high as 1050 to 1100° F. (560 to 600° C.) and we stayed with a steady calcium of about 26 parts per million. Then we got a very high calcium raw sugar and went up to 50 parts per million.

F. G. Carpenter: In that case you will have to use more wash water.

J. F. Dowling: Then it becomes an economic problem of how much wash water you can add to take care of the calcium removal.

F. G. Carpenter: The work you cited pointed out that the calcium level in liquors off char was very much dependent upon reburning temperature, and only somewhat dependent upon calcium not washed off char in the previous cycle. If your calcium level in liquors off char is going up too high, then you very plainly must either wash more, or reburn at a higher char temperature. What you do is a local problem because each refiner has a different temperature capability, time schedule, or water supply problem or some other bottleneck. I can give you the guidelines which will tell you which way you will have to go but how far you have to go is up to you individually.

(1) Carpenter, F. G., Larry, D., and Deitz, V. R., Proc. 7th Tech. Sess. Bone Char 1961, p 259; also Bone Char Tech. Report No. 69 (1962)

T. M. Rinehart (Atlas): Some years ago Dr. Rice of Inland Sugar put in a bone char installation including a rotary kiln. It turned out that all the carbon was burned off the bone, yet it was reported that the material was still doing a very excellent job of decolorization. Would you care to comment on that?

G. W. Muller: Well, I believe it has been shown that carbon isn't necessary for decolorization. I can remember an example of the segregation of the white char from broken retorts. We filled a char filter full of this young decarbonized service char. We washed and drained it, then ran soft liquor on it, and compared it with the best grade of char from which that white char came. Decolorization of the soft liquor was excellent. Carbon was nonexistent on that material so the hydroxyapatite does adsorb many colors without having to have the carbon. However, carbon on bone char does do a job for many of us.

P. F. Meads (C&H): We had some laboratory experience with white char some years ago and white char does adsorb some color. However, at the other extreme it has been said that the carbon content of service chars should be equal to, or less than, that of new char. Our carbon content is appreciably higher. We have a feeling this isn't right, but we can't find any direct evidence that will tell us that this isn't right, or how bad it is. I wonder why the statement was made that carbon content of service char should be equal or less than that of new char.

F. G. Carpenter: We have found on several occasions that if you build the carbon content up a little then you are covering over the entire surface with a newly formed layer of carbon. In many cases the new surface seems to be less "active" than the virgin carbon. This is proven by the fact that if you do decarbonize ever so slightly, then the char gets better. As an extreme case, I once saw bone char at 34% carbon. It looked like anthracite coal and wasn't doing anything. We decarbonized that all the way down to 6% and it then decolorized just like it should have.

P. F. Meads: I think that we might speculate that this does happen, but if you watch the carbon on service char increase for several years and the batch decolorizing test results hold level, you wonder what's going on.

F. G. Carpenter: It would seem possible that a little bit of carbon could be well placed and well reactivated, and thus the carbon content could be built up. Don't forget that when you keep the carbon content constant you are actually building it up. You start out with 40 pounds per cubic foot char and you adsorb a little ash in it, which you don't wash out but instead burn in. This ash increases your base and in order to keep the carbon constant you must add carbon too. True, this is a very small amount, but it still seems to stay just as active. You were either fortunate or skilled in regenerating it properly.

P. F. Meads: In passing over decolorizing resins I think you said that the beds would have to be replaced after 70 cycles. I am a little bit surprised that some of the resin people haven't responded to this, since this seems to be a very low life for these resins.

G. W. Muller: I was simply quoting one refinery's experience on a decolorizing resin. I know that resins have much longer life for other purposes, but this was a decolorizing resin.

Another thing on this black and white bone char, some refineries have successfully gotten carbon to build up on their bone char by underwashing and overloading. It looks as though they were lucky in their regeneration. They could build the carbon up from very low to nearly normal and get a better decolorizing char.

R. J. G. Macdonald (British Charcoals): Mr. Muller does stress, and I think very rightly, that the Kip Kelley is a very necessary piece of equipment in a sugar refinery to take away the heavy nonactive particles. This

was borne out both in Table 2 and in the photographs by Mike Bennett.

In regard to the question of the carbon going upwards and downwards, we have done a lot of experimentation on this and have believed that the added carbon is a non-active carbon which will give some decolorizing power but will not give the same decolorizing power as the original carbon that is burned into the bone from manufacture. I would agree with George that the carbon content should stay around the level it starts out, be it 8 or 10%. If you go upwards you are adding nonactive carbon. If you go downward you are losing carbon, and you are more likely to lose the active carbon than the nonactive. You will get decolorizing power but you won't get the same activity.

G. W. Muller: Thank you. I agree with you on that.

R. S. Patterson (C&H): You mentioned that you can both overburn the char and underburn it, and you also mentioned that it's the truth that many refineries don't watch this too closely and don't have proper control over it. They either are going to overburn or underburn the char and, in your opinion, would 10% overburning be better than 10% underburning?

G. W. Muller: I feel that it is better to have a little overburning. You are looking for a high pH. If the crystallites do grow and become hard, you have a means through the SS&S to get rid of old bone char. However, if you do get underburning, you can bring it back to within reason by a controlled atmosphere of oxygen to get off that excess carbon that may build up and may be less active.

W. A. Bemis (Revere): European chars generally run a little higher in carbon than American chars. In Europe they use something like 10% while in the United States it is nearer 5%. Now I personally subscribe to the view that whatever the initial carbon content is, it is better to keep it no higher than that. So the question now arises if you are buying some char, why should you want 10% carbon when 5% carbon might do the same job provided you don't permit either one of them to rise above their original level. I believe that it has been shown that the activity of the char is not related to the initial carbon content, but to some relation between the surface area and the carbon content.

G. W. Muller: I don't think it makes any difference what the original carbon content is because the refiner immediately begins to modify the carbon. It may go up and it may go down. It becomes the refiner's char within a very few cycles. The carbon content has been related to decolorizing but it isn't the only criterion of good char any more than the surface area or hardness. Each one has some bit of influence upon decolorizing ability. Whether carbon is the predominant decolorizing agent, the hydroxyapatite, or the open pores, or the high surface, is not known. The amount of carbon in bone char is very low and its surface area is very high, almost in the class with the granular or powdered carbons when based on carbon alone. We never did quite get these answers from the Bone Char Project. I think we quit ten years too soon.

R. J. G. Mcdonald: I am hoping that these new tests that Tate and Lyle instigated of CTAB and OT will teach us a lot more about the carbon surface area, and even hoping that they will be able to be related to the decolorizing power through a column test. These tests are not really very strenuous tests but admittedly you couldn't do them every day. I think they could be done at three monthly intervals to give a check to make sure that the char is behaving well or going upwards or going downwards, and one could take steps to counteract that. I really hope that these tests are going to teach us a lot.

G. W. Muller: I hope so too.

E. J. Culp (American): Going back to Dr. Meads comments about high carbon and good

decolorization, perhaps we should think not in terms of the level of carbon content, but of its trend. The situation might be compared with a marathon race where, at the end of the race, the energy we have left for the last spurt depends upon whether we were running fast or slow during the first part of the race. So, too, with carbon. If we had been building up carbon, remember, the carbon we build up may not be so good in quality, and that carbon is likely to be located at the pores near the outer surface of the particles and in the larger pores, which is exactly the site that is accessible to the color bodies. In that case, we are liable to find poor quality. However, at the same carbon content, if we have been high in the past but are coming down, then we will find that we have burned off the poor carbon that we deposited in the larger pores and toward the outside. The poor carbon that is left is way on the inside where it is inaccessible to the color bodies and we are likely to find good quality. So, perhaps, there is a statistical explanation for these differences even at a given carbon content.

T. M. Rinehart: It is interesting that the glucose people build the carbon up and the cane sugar people build it down.

PITTSBURG TYPE CANE-CAL IN MOVING BEDS AT EMILIANO ZAPATA

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INTRODUCTION

Any time a refinery converts from one process to another and from one set of equipment to another, the results of the first year of experience are usually anything but conclusive. Mechanical and process start-up difficulties will cloud analyses and prevent drawing of meaningful economic evaluations. This is especially true in those areas where the new installation is to be used on a crop basis. The crop at this refinery extends between 150 and 190 days. The granular activated carbon decolorizing unit which I shall describe, is unique in that there were no equipment or process failures or difficulties respectively. I shall describe the problems encountered subsequent to start-up and the remedial actions taken.

On Thursday, 18 January 1968, Mr. Marc Antonio Munoz, general manager of the refinery "Emiliano Zapata" in Zacatepec, Mexico opened the 6-inch valve to begin the liquor flow to the 30th Granular Activated Carbon System employing Pittsburgh Granular Activated Carbon for the decolorization of cane sugar. Seventeen of these thirty installations are Pittsburgh Moving Beds and thirteen are fixed beds. This mill - refinery is using the system of Moving Beds of Type CAL, admixed with 5% by weight of dead-burned magnesite. The liquor to the columns is maintained at a Brix of 60° ± 1. The liquor has been defecated with phosphoric acid and lime, clarified through Jacobs Clarifiers, and polished filtered through pressure filters which are on hand from the previous refining operation.

DESCRIPTION

The filtered, clarified liquor is pumped to the decolorization station at a rate slightly in excess of 550 metric tons per day (600 short tons). This delivers approximately 35 g. p. m. to each of the four carbon towers. Each of these is 8 feet in diameter with a straight side height of 30 feet. The bottom cone is angled at 45 degrees while the top cone has a 30 degree slope. The two cones add approximately 3 feet to the effective bed depth. The total transit time through each column is 3 hours 45 minutes. The liquor at 60° Brix, 7. 1 pH, 6. 5 Horne Color, and 185° F. passes upward through

the carbon bed removing between 75 and 85 percent of the influent color, during the passage. I have fixed the pH at 7. 1, since this was the pH of the liquor I observed at start-up. While influent pH dropped below neutrality from time to time, the refinery was meticulous in monitoring the system, making adjustments as needed. Treated liquor was trap-filtered for clarity and the removal of fines. Filtered liquor, of course, was sent to the evaporators. Spent carbon (0. 53 apparent density) is slugged through a manually operated eight-inch ball valve, and is transported hydraulically through a two-inch eductor pump to one of two slug receivers (blow cases). Spent carbon is again transferred to one of the two sweetening off columns, using air.

Spent carbon, sweetened off to 1° Brix and washed for two hours, is pressurized to the regeneration module. The reactivation station has a classical profile. The dewatering tank of five feet diameter and thirteen feet from the top to a slide gate valve is located immediately over the kiln feed hopper, itself positioned immediately over the regeneration furnace. The feed hopper is 7. 5 feet in diameter and 13 feet high including the 60° cone. Carbon flow from the hopper has two controlling mechanisms. One is a slide gate valve, manually operated, which is left in the open position during the regeneration. The gate is closed only when a charge from a dewatering hopper is dropped to the kiln feed hopper. The second controlling mechanism for carbon from the hopper is a small Vari-Feeder belt with level controlling drop gates. The belt, in turn, supplies the hopper to the rotary air-lock valve to hearth No. 1. Both the dewatering tank and kiln feed hopper are equipped with vibrators. The kiln, of Bartlet Snow Pacific manufacture is the Herreschoff type, 54 inches I. D. six hearths, and fired on hearths Nos. 4 and 6. There are two burners per hearth, using diesel fuel. Each firing hearth has been equipped for the injection of steam as an atmosphere controlling agent. The steam usage is approximately 0. 5 pounds per pound of regenerated carbon. Kiln operation is automatically controlled from a panel positioned, unfaithfully, adjacent to the regeneration station. The burners are fired automatically with pilots using butane gas as fuel, and ignited with spark plugs. Each burner has been equipped with manual controls as well as a purple peeper set at a 45° angle to the burner orifice.

Regenerated carbon drops through an eight-inch-water-sealed down line to a quench tank. I found the sample leg affixed to the under side of the down line too short (10 inches). At my suggestion they are lengthening this to three feet with double valves to prevent atmospheric blow-back to the kiln and potential operator injury.

The kiln product from the sample leg, screened to eliminate the fine particles of dead burned magnesite, has averaged 0. 475 g/cc. apparent density over the period of usage during the latest crop.

The kiln product at 1700° F. (900° C.) drops into a quench tank which is four feet in diameter and, including the shallow cone, 6. 5 feet in overall height. The product line into the quench tank is maintained at a water-sealed condition by a float valve on an auxiliary water line. A three-inch water line to the quench tank maintains a suspension of regenerated carbon, and works as a fines removal agent. Floating fines flow from the quench tank through V-notch and are drained through a strainer which catches any granular carbon overflow. Quench tank slurry is returned to the slug feed hoppers by either one of two ceramic lined centrifugal pumps.

The slug feed hoppers are five feet in diameter and eight feet high including the 60° cone. These hoppers are equipped for washing and fines removal by means of a cylindrical screening arrangement which retains granular activated carbon, while permitting fines to pass through to waste. Regenerated carbon is slugged to the working columns through a three-inch ball valve, manually operated. The feed slugging operation is begun immediately after closing the eight-inch valve at the bottom of the columns.

A uniformly packed bed will provide the optimum liquid-solids mass transfer conditions. This is especially true and necessary in an upflow operation. A two-inch water line with 20 p. s. i. g. water rings the down line from the ball valve of the slug feed hopper. This was installed to help maintain as complete a filling of the carbon columns as possible. Eight lines of one-inch diameter go directly through the head of the columns from this two-inch ring. In a matter of seconds, any hump of reposed carbon is leveled, permitting the addition of enough carbon to provide the required static bed. That this procedure is successful was proven in the start-up preparations. The carbon columns were brought to operating temperature with 185° F. (85° C.) water at 1 g. p. m. per square foot. I halted water feed operations to each of the four columns in turn and checked for freeboard in each column. After allowing one hour for settling time, two of the columns were completely full. We estimated that columns No. 2 and 4 took an additional five cubic feet per column to reach the packed condition.

Mr. Raul Dominguez, chemical engineer and refinery superintendent, his able staff of engineers, and Mr. Lazaro Cardenas, general contractor, had done their work extremely well. All four units, auxiliary equipment, and the regenerating equipment performed beautifully from the time the main valve was opened.

OPERATING RESULTS

Slugging operations worked extremely well, as long as beds were maintained in a fully packed condition. Subsequent laxity in observation of bed level permitted enough accumulation of freeboard, so that the bed became partially fluidized. The denser-than-carbon mangesite (120 lb. /cu. ft.) partially settled out and began the formation of conglomerates of carbon and magnesite. None of the conglomerates, however, were large enough to block completely the eight-inch aperture through the ball valve. However, the eductor pumps were disconnected several times, so that magnesite-carbon balls could be removed. One small conglomerate passed through the eductor pump, completely through the regenerating station, until it arrived at one of the ceramic lined centrifugals. A new pump had been installed, as of my system follow-up visit in July of this year. Another effect of magnesite drop out was noticed in the drain connection on the distributor line. When the bed is slugged (pulsed), there was a feed-back through the distributor heads (well point shutter screens). Some of it remained. The problem of magnesite-carbon conglomerates and magnesite drop out will be eliminated next crop with the introduction of Pittsburgh Type CANE-CAL 12 x 40 Mesh. This carbon, as some of you know, has the particles of magnesite bonded into the matrix of the carbon granules. In addition to the elimination of the conglomerates, CANE-CAL will provide them with much better control of pH and invert. For these reasons, fifteen out of the thirty granular activated carbon installations have converted to this type of Pittsburgh Carbon.

The sweetening-off operation gave excellent results. The sweetening-off tanks are five feet in diameter and nineteen feet on a straight side. The bottoms are coned at 45°.

The sweetening-off water is introduced down-flow at a rate of 0. 1 g. p. m. per ft.^{2}. They use three volumes (6 hours) to bring their sweet water Brix down to 1°. They would use slightly less (approximately two volumes) to sweeten-on these columns in an upflow operation.

Dewatering and kiln feed operations went along in a completely trouble free manner. The regenerating kiln delivered a fairly consistent product ranging between 0. 460 and 0. 490 apparent density. The average of 0. 475 apparent density is an excellent service carbon.

ECONOMIC EVALUATION

The refinery superintendent of Ingenio Emiliano Zapata reported a saving of

$61,916.97 over 95 days. He went on to say, "It is evident that in this first year of operation of the Pittsburgh Refinery we absorbed some losses of carbon produced in the transportation and handling of it from its point of origin to the columns." Mr. Dominguez went on to say, "Knowledge of the operation of this plant will, in the future, permit a reduction of operating personnel."

Let's take a look at these costs and savings. Remember, extra supervisory labor costs, power and fuel, chemicals, and the cost of completely regenerating all of their spent and partially-spent carbon at the end of the crop have gone into the start-up charges.

First, let us go back to the 1966-1967 crop of 166 days, when 82,000 metric tons of sugar were produced.

1966-1967 CROP - 166 DAYS

Sugar Produced (Metric Tons)		82,000
Vegetable Carbon Used, Kg./mt.		4.15
Vegetable Carbon Use, Kg.	Total	340,300
Vegetable Carbon Cost, Dl'vd	Total	$137,000

You will notice that the carbon dosage is 4.15 kilograms of pulverized activated carbon per metric ton. The vegetable carbon usage, therefore, in kilograms totaled 340,300. The total cost of the delivered carbon was $137,000.

Their Pittsburgh Granular Activated Carbon System operated for only approximately 3/5 of the 1967-1968 crop.

1967-1968 CROP - 95 DAYS

Sugar Produced (Metric Tons)		49,000
Granular Carbon Used, Kg./mt.		.434
Granular Carbon Use, Kg.	Total	21,000
Granular Carbon Cost, Dl'vd	Total	$15,373

The actual usage of granular activated carbon for these 95 days totaled 21,200 kilograms. Notice that the carbon usage was only .434 Kg./mt, even while absorbing, warehousing, and start-up losses. The delivered cost of this quantity of carbon totaled $15,373.

I have extrapolated all costs considerations to meet a 166 day crop which produced 82,000 metric tons of refined sugar.

82,000 METRIC TONS, 166 DAYS

Veg. Carbon Cost	$137,000
Gran. Carbon Cost	26,000
Saving	$110,000
Less Start-up Charges	15,400
Total Saving	$94,600

It is expected that the savings will accumulate at the present rate through next year. The 1969-1970 crop will surely see a significant drop in the cost of labor and final regeneration. Good planning, heads-up engineering, and meticulous process control will be responsible for the return of 100 percent of invested capital, including interest, by the end of the fourth crop. This is an excellent return in investment in any country.

DISCUSSION

H. G. Gerstner (Colonial, USA): Do they use series or parallel flow?

F. M. Williams (Pittsburgh): They use parallel flow over four columns. One pass through the columns. Three hours and forty-five minutes contact time.

H. G. Gerstner: Did they try series flow?

F. M. Williams: No, they didn't try that.

H. G. Gerstner: If you were to design a new refinery, what changes would you make in a new operation over the present one?

F. M. Williams: I would not use an admixture of carbon and magnesite. I would use CANE-CAL carbon. I would also increase the angle of the cones at the bottom of the operating columns to get a better slugging operation. It is thought that there may be a considerable length of ratholing in those

moving bed columns. We find that a very steep cone will minimize this. The Japanese (1) have actually done some work putting layers of white quartz in layers with carbon in the column and they found 13 slugs later all the quartz had slugged out. So the beds drop on a fairly level basis until they get close to the bottom and the cone. Then there is an involution and a short rathole.

S. Stachenko (C & D): From the figures you have quoted on the savings, can we conclude that the cost of the installation was about $400,000?

F. M. Williams: Yes, that is about right.

R. A. Hutchins (Atlas): What was the level of decolorization by the previous method, using powdered carbon, compared to the level of decolorization using the granular carbon? And, also, what were the pulse rate and the pulse volume?

F. M. Williams: They were pulsing 110 cubic feet, once a day each column. I do not know how the decolorization compared with their previous method using powdered carbon. At present they are reporting a satisfactory removal of 75 to 85% of the influent color. The final sugar is around 0.6 Horne. They are getting 0.02 to 0.03% Ash, but this passes Mexican specifications.

R. J. G. Macdonald (British Charcoals): Can I ask the difference in density between CANECAL carbon and ordinary CAL carbon?

F. M. Williams: They are exactly the same density.

E. J. Culp (American): Was the desweetening operation accomplished by downward flow or upward flow?

F. M. Williams: It was downward flow.

P. Petrie (Godchaux-Henderson): Do you have any figures on the losses through the pulsed bed, and any comparisons with a fixed bed?

F. M. Williams: Their rate of burn or burn ratio ran around .9 and their kiln gave them slightly less than 5% losses. This is excellent in the first year of operation. Their carbon purchases came out to be 0.434 kilos of carbon (2) per metric ton of sugar produced. In a properly operated fixed bed operation, for instance at SuCrest, they once had a .33 or .35 burn ratio. The kilns were returning about 4%, sometimes slightly more than 4%, losses. (3) The carbon replacement ratio, therefore, was about .012 lbs of carbon per bag of sugar.

P. Petrie: How about sucrose losses; do you have any figures on that?

F. M. Williams: No, I have no figures on sucrose losses. In Mexico they put out a large sheet or "corrida" which goes to the government at the end of the year, but in no place do they report sucrose losses to the adsorbent. They report sucrose losses to bagasse, inversion, molasses, etc., but they don't seem to bother with losses to their carbon.

T. M. Rinehart (Atlas): I would like to make a few remarks in this connection. Great Western Sugar Co. ran some tests with granular carbon and they found that when the carbon was unspent, that is, it hadn't been used at all, they got a high sucrose adsorption. But, as the cycle went on, the adsorbed sucrose was replaced with nonsugars, so they ended up with a very low retention of sugar, down to about 2% on spent carbon at the end of the decolorizing cycle. I know that Frank Carpenter has done work in the past where he showed about a 6% retention of sugar, using pure sucrose. Great Western's results were rather interesting, particularly since they too used a 20-foot column.

(1) Miyahara and Suzuki, Japan Organo Co., Ltd. 1965
(2) Informe Sobre La Operacion De La Estacion Decoloracion Con Carbon/Granular "Pittsburgh" Durante La Za Fru, 1967-1968. Ing. Raul Dominguez Morales, June 5, 1968, Rpt.
(3) Fred Bruder, SuCrest Corp. - Publication of Symposium of the Twenty-Second Annual Meeting, Sugar Industry Technicians, Inc. May 17, 1963

THE POROSITY OF ACTIVATED CARBON AND ITS RELATION TO CANE SUGAR REFINING

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INTRODUCTION

Everyone is generally aware that activated carbon derives its ability to adsorb impurities from sugar solutions as a result of its large surface area. Because of the familiarity of the use of carbon as a powder, it is sometimes thought that this large area results from the finely sub-divided state of the material. Generally speaking, powdered activated carbon has a typical particle size on the order of 40μ in diameter. Considering these particles as spheres, we can calculate an external surface per unit weight equal to 0.150 m.^{2}/g. However, measurements of surface area of activated carbon give values much larger than this, i.e., in the order of 600 to 1700 m.^{2}/g.

The reason for this considerable difference is that activated carbons are considerably porous. These carbons have on the order of 0.85 to 3.0 ml./g. of pore volume inside the particles, and the extensive surface area is located internally as walls of these pores.

The purpose of this presentation is to review the basic concepts that relate carbon porosity to various processing steps. These processing steps are: (a) color removal with carbon which can involve the use of either powdered carbon in a batch operation, or granular carbon with a continuous flow; (b) the entry of sucrose into the carbon pores, a step which is commonly referred to as "sweetening-on"; (c) the "sweetening-off" operation, where the sucrose is recovered after the carbon has performed its purifying job; and (d) the processes that regenerate spent carbon where there is a definite relationship between effective restoration of absorptive capacity and carbon porosity.

MEASUREMENT OF POROSITY

Current experimental methods of measurement of porosity give a description of this property in two ways:

1. The total volume of pores.
2. The distribution of this volume among pores of different radii.

Total porosity is measured by mercury and helium displacement techniques (1). Mercury does not wet carbon. Therefore, the volume of mercury displaced by carbon equals the volume of carbon and the volume of its pores. Helium will penetrate into the pore structure without appreciable adsorption at room temperature and will be displaced only by the carbon. Thus, the volume of solid carbon is measured. Subtracting these two volumes gives the volume of pores. Making these measurements on known weights of carbon, we can obtain the volume of pores per unit weight.

The measurement of the distribution of pore volume among pores of different radii is obtained by forcing mercury into the pores (2). The volume intruded at each increase in pressure is measured. The pore radius intruded at a given pressure is given by

$$r = \frac{-2\sigma \cos \theta}{P} \quad (1)$$

Where

r = pore radius,
σ = surface tension of mercury,
θ = contact angle between mercury and carbon (assumed to be 140°),
P = pressure.

In convenient units equation 1 becomes

$$r(\text{in Å}) = \frac{106 \times 10^4}{P(\text{in psia})}. \qquad (2)$$

According to this equation, pores with a radius of 20 Å can be penetrated by applying a pressure of 53,000 p. s. i. a. The equipment for these techniques has been described in the literature (3, 4).

In the pores less than 100 Å radius, the pore size can also be determined by saturating the carbon with liquid nitrogen at boiling liquid nitrogen temperatures (-195° C.), and then measuring the amount desorbed at decreasing pressure increments. The amount of desorbed nitrogen is a measure of the pore volume. The pore radius is given by the Kelvin equation after correction for adsorption other than capillary condensation, i. e., layer adsorption (5). Calculations are not extended below pores of 20 Å radius because the relation is considered inapplicable.

Presentation of the data is shown in Figure 1 in the form of a bar-graph. Each bar represents a given pore radii increment in logarithmic units. The height is the volume of the pores in the given increment. In order to illustrate how widely carbons can differ in their structures, graphs are presented for a typical cane sugar carbon and a typical gas carbon. Note the differences are as follows: a cane sugar carbon has considerably more pore structure in large pores, in contrast with a gas carbon which exhibits more fine pores than a cane sugar carbon.

The significance and necessity of this type of structure for a cane sugar carbon will be discussed later. It is beyond the scope of this paper to deal with the structural significance of the gas carbon, but it might be mentioned in passing that the adsorption of gas is greatly enhanced by a fine pore structure.

COLOR ADSORPTION AND POROSITY

In the case of adsorption of substances from a vigorously stirred solution at a readily accessible solid surface such as a planar interface, equilibrium can be obtained in a very short time span, on the order of a few minutes. However, with an activated carbon, a significantly longer time is required. The difference is accountable on the basis of the porosity of the carbon.

Fundamentally, an effect on the free diffusion of substance in a pore occurs when a pore radius is small enough and the pore path sufficiently erratic that the chance for a molecule to collide with the pore wall rather than traversing its normal mean free path is greater.

In the case of color body, it is not possible to decide from these fundamental considerations that the free diffusivity has been affected because the mean-free path is unknown. However, adsorption of pure compounds from solutions has shown that the rates of diffusion into the pores is less than that found when conditions for free diffusivity exist (6, 7). Thus, it is reasonable to expect that the pores of carbon make up a diffusion barrier for the color bodies.

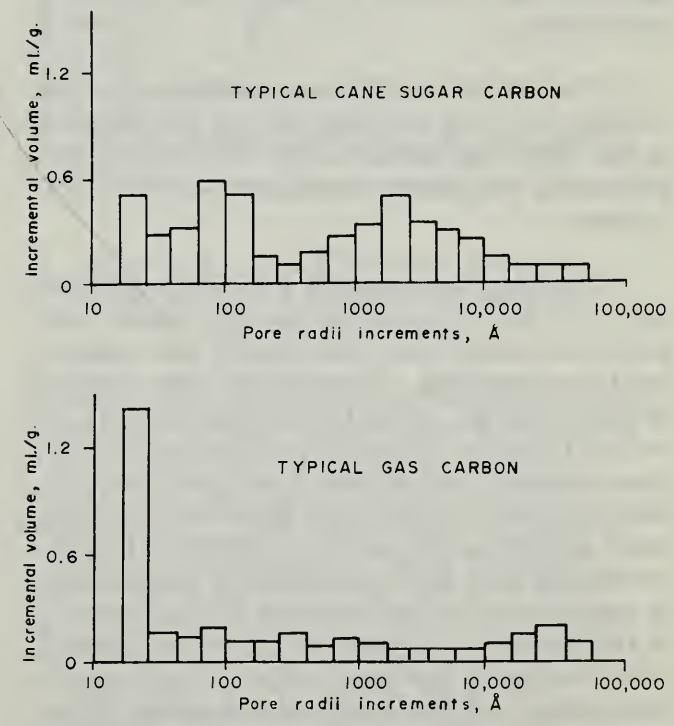

Figure 1. Pore Volume-Radii Distribution

A variety of equations have been derived for relating the various factors affecting the rate of adsorption by porous substances. Most of these are complicated. However, an empirical equation which is more simple, and related in form to the others, is as follows:

$$\ln \frac{Ct}{Co} = - \frac{Co-Ce}{Ce} \frac{VD^{1/2}t^{1/2}}{WPR} .$$

Where:

C_t = concentration at time t,
C_o = initial concentration,
C_e = concentration at equilibrium,
V = Volume of solution,
W = weight of carbon,
P = porosity per unit weight of carbon,
R = radius of particles,
D = "effective" diffusion coefficient,
t = time.

This relation is applicable to batch treatment and describes the course of adsorption to about 85% of equilibrium. This simple form aids in pointing out the effects of various factors, particularly porosity, on rate of adsorption.

The effective diffusion coefficient of the system, D, is a function of: (a) the character of the diffusion species, (b) solvent, (c) temperature, and (d) structural character of the carbon.

Porosity is obviously evident in the factor, P, i.e., the greater the pore space into which diffusion must take place, the longer the time required. Porosity is also involved in the factor D. Recall that this was referred to as an "effective" diffusion coefficient and was considered a function of a carbon structure because the adsorbed species must diffuse in the pores. Diffusion theory maintains that the free diffusion coefficient is limited in a direct manner by the radius of the pore (8). Referring again to Figure 1, note that there are pores of all sizes, and according to diffusion theory, a given diffusion rate constant should correspond to each size. However, actual data suggests that there is an average behavior. The pore distribution of the typical carbon does not exclude the possibility of an average behavior, because within certain ranges there are dominating sizes. Thus, an approach to this "maze" of pores would be to consider the distribution around each maximum as statistical and acting collectively as its mean pore size.

It is reasonable to expect that the mean pore size corresponding to the peak in the range of large pores would be the main channel to the smaller pores.

To illustrate the dependency of the rate of adsorption of color from sucrose solution on porosity factors, plots of the fraction of color remaining (Log scale) as a function of the square root of time for four different carbons are shown in Figure 2. Also, pertinent data for Figure 2 are tabulated in Table 1.

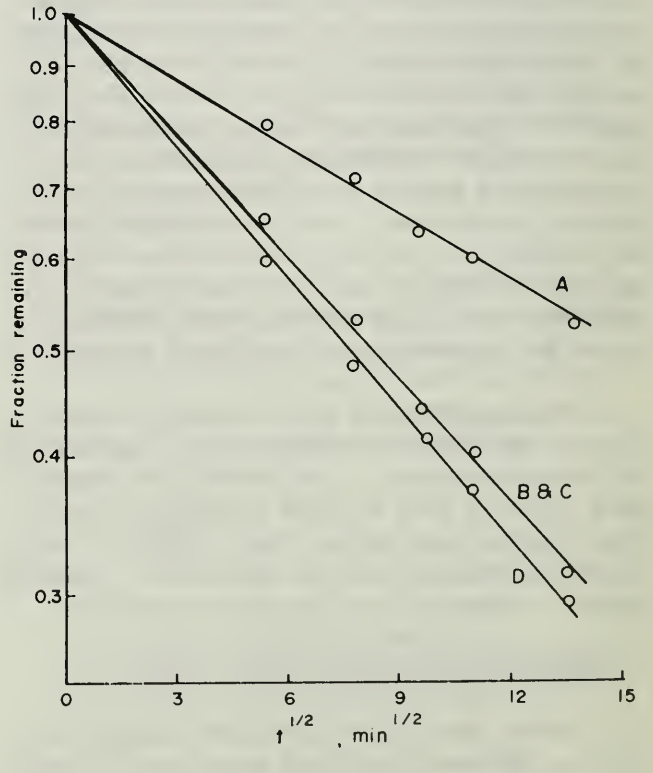

Figure 2. Time Dependence of Color Adsorption

Table 1. --Data Pertinent to Time Dependency of Color Adsorption Illustrated in Figure 2

Carbon[a]	$\frac{C_e}{C_o}$[b]	Porosity, ml /g	r_o,[c] Å	Slope $min^{-1/2}$	D,[d] $cm^2/min \times 10^{11}$
A	0.040	0.80	9000	0.048	7.0
B	0.023	0.84	9000	0.095	8.0
C	0.011	0.89	2500	0.095	2.0
D	0.013	0.97	5000	0.099	3.0

[a]Granular samples, all with about the same average diameter of 0.95 mm. 100 ml. of syrup were treated with 1.0 g. of carbon.
[b]Fraction remaining at equilibrium
[c]Average radius of macropores.
[d]Effective diffusion coefficient.

The carbons were used in granular form in order that timing would be longer and not so critical. With powdered carbon, the particles are so small that color removal is rapid and timing of the experiment must be very precise. This is evident from equation 3. Obviously, under practical circumstances, a powdered carbon would be used in a batch contacting system because a more rapid equilibrium is obtained as a result of smaller particle size. However, particle size and porosity are not inter-related and what can be shown for porosity effects for a granular carbon is true for the powdered counterpart.

The set of carbons were of the same particle size, mainly 12x40 mesh, but varied according to: (a) adsorptive capacity at equilibrium, (b) total pore volume, and (c) mean pore radius of the macropores with the exception of carbons A and B. Using equation 3, the effective diffusion coefficients for each were calculated and are tabulated in Table 1.

The relationship of D to r is illustrated in Figure 3 where increasing macropore size corresponds to an increasing effective diffusion coefficient.

In granular carbon beds, the mathematical description of color removal is considerably more complicated. It is a non-equilibrium process controlled by diffusion, and the

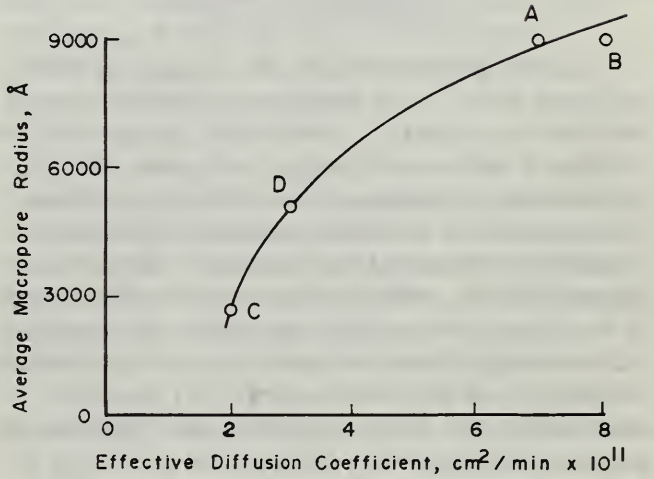

Figure 3. The Effective Diffusion Coefficient as a Function of Average Macropore Radius

variables discussed in connection with batch contacting likewise apply. One approach is to consider the bed as a set of batch contactors with the liquid flowing through in sequence (9). Color removal as a function of time is established for each contactor. This relation also includes the time when the unit reaches equilibrium adsorption of color from the influent liquor and thus can be considered as "dropping out of line". Currently, the relation is established empirically for a given carbon by a pilot column length. Color of the effluent for small

increments of flow through the set of contactors is calculated, and thus a color concentration profile is established for the set, with sequential loss of units from the line.

The relation of color removal to time in the contactors of this system differs basically from that shown in equation 3 because here the color concentration of the liquid continually increases, while in a simple batch contactor, it decreases. Workable equations, particularly those taking into account the variables involving structural characteristics of the carbon, are not yet available. Atlas is currently pursuing a program to develop such relations.

RELATION OF EQUILIBRIUM ADSORPTION TO SURFACE AREA

It was pointed out in the beginning that carbons have large surface areas because of extensive porosity. Obviously, large surface area is a necessary property for an efficient adsorbent. However, the extent of surface area cannot be used as a measure for the equilibrium adsorption of color. To obtain a quantitative relationship between the extent of surface area, and the quantity of material collected at this solid interface at equilibrium, requires that the fraction of total surface covered by the color species as a function of its concentration be constant for all types of carbon and all kinds of color species.

There are a number of circumstances that prevent this. These are as follows:

1. All of the surface of a carbon is not necessarily available for adsorption because molecular size prevents certain substances from entering small pores. Carbons differ in their structural character and thus, what may be termed "spatial inhibition" to the covering of the surface will vary among carbons.

2. The chemical nature of the surface can vary among carbons. This chemical nature usually involves the amount and type of bonding of oxygen, which can definitely affect the extent of coverage.

3. The amount of material adsorbed will be affected by how the molecules orient at the surface and how closely they pack against one another. Studies with pure compounds have shown that this is a function of molecular structure and concentration (10). Thus, with the possibility of a wide variation in the amount and types of color species for various sugar liquors, considerable variation in the extent of coverage from type to type can be anticipated.

4. Study of pure compound adsorption has shown some preferential adsorption of various molecular types over others. Therefore, when these types are mixed, a competitive situation arises and the extent of surface coverage is governed by the relative amounts of different materials in the mixtures. This type of variation is quite possible in different kinds of sugar liquors.

SWEETENING-ON

When carbon is first brought into contact with the sugar liquor, a point of interest is, of course, to minimize dilution of the sugar liquor. When operating with powdered carbon in a batch system, this is no particular problem because the amount of water brought into the process by the carbon, as its natural moisture content, is small. This moisture content arises from the fact that cane sugar carbons are sufficiently microporous to have some efficiency as vapor adsorbing carbons. Therefore, they adsorb moisture from the air. Since it is not practical to deliver carbon and handle it under absolutely dry conditions, there will be some moisture content. Ordinarily, this is of the order of 5-10%, but for some carbons can be as high as 25%, However, powdered carbon dosages are small, and thus no appreciable dilution occurs.

In granular carbon systems, the possibility of dilution is greater because at the time of introducing sugar liquor to the bed, the carbon particles are saturated with water as a result of being conveyed to the column in a water slurry. Thus, the sucrose will diffuse from the concentrated external liquor into the water contained in the pores. Therefore, the concentration of sucrose in the pores increases while that in the external solution decreases. This process will have some time dependency because of diffusion control. The effects of porosity on the time dependency of color adsorption, which have been described previously, apply as well to the diffusion of sucrose into the pores.

Of course, it is normal practice to sweeten-on under flow conditions rather than in a batch process. However, a comparison of the extent of dilution of sugar liquor when sweetening-on in an equilibrium batch process, with the dilution obtained under non-equilibrium flow conditions, reveals how limited diffusion in pores results in less dilution of sugar liquor under flow conditions.

The dilution obtained in an equilibrium batch process for a cane sugar carbon having typical values of bulk density, void space of bed, and pore volume can be calculated as follows:

1. Amount of carbon per cubic foot of bed = 24 pounds.

2. Amount of water in bed assuming a pore volume of 0.9 ml./g.
$= \frac{0.9 \text{ lb. of water}}{1.0 \text{ lb. of carbon}} \times 24 \text{ lb. of carbon}$
= 21.6 lb. of water.

3. Amount of void space in carbon bed = 0.5 cu. ft.

4. Amount of 60 Brix sugar solution (80 lb./cu. ft.) in void space = 80 lb./cu. ft. x 0.5 = 40 lb. of solution
40 lb. x 0.6 = 24 lb. of sugar solids

5. Brix after equilibrium
$= \frac{\text{Sugar Solids} \times 100}{(\text{Wt. of Solution}) + (\text{Wt. of Water})}$
$= \frac{24 \times 100}{40 + 21.6} = 39.0.$

Time for equilibrium would be relatively short-on the order of one to three minutes. This may seem rapid. However, referring to the equation 3, the value of the group V/WP, representing the ratio of external volume to pore volume, is small because the ratio of carbon to liquid is large. As the ratio of carbon to liquid is increased in a system, the rate of diffusion becomes more rapid. Thus, sweetening-on under equilibrium conditions results in 0.5 cu. ft. of 39% sugar solution per one cubic foot of carbon bed, or, considering a typical carbon bed occupying a volume of 15,000 gallons (2000 cu. ft.), 7,500 gallons of 39% sugar liquor would be produced.

The complications and present limitations of a reliable mathematical approach to non-equilibrium adsorption of color from sugar liquor flowing through beds of granular carbon, discussed earlier, also apply to diffusion of sugar into and out of carbon. However, recognizing the limiting aspects of diffusion in pores, it is reasonable to expect diffusion control under flow conditions.

Therefore, it is reasonable to expect that under typical refinery flow rates of 0.2 to 0.4 bed volumes per hour, the concentrated sugar is moved past the carbon particles at a rate fast enough to prevent equilibration. Thus, less dilute liquor is produced. This is illustrated in Figure 4. The data is from a laboratory column study. At the beginning of upflow, the carbon and bed were saturated with water. The first outflow is water being displaced by the upward moving denser sugar liquor. This would amount to one void volume. The next 0.4 of a void volume is very dilute sugar liquor produced as the result of this particular volume's passing entirely through the column and the sugar within it

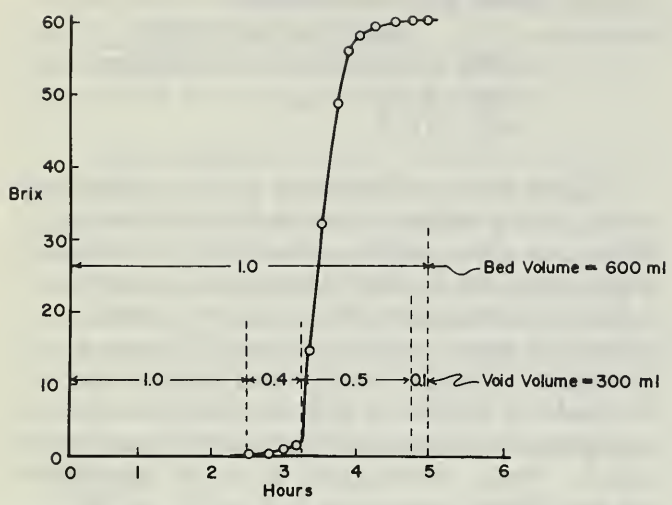

Figure 4. Sweetening-on 12x40 Mesh Carbon

diffusing almost completely into the carbon pores. During this process, the sugar concentration in the pores has increased, thereby decreasing the rate of diffusion into the pores because the concentration difference between the external and internal solution has decreased. Next, a sudden rise in concentration is noted within the passage of 0. 5 void volumes; the concentration rises suddenly from 1 to 60%. Thereafter, it remains at 60% for another 0. 1 bed volumes.

If all of the volume in the 1 to 60% range was collected together, the final concentration of this volume would be 47. 5% sugar. Placing this 0. 5 void volume on the basis of the 15, 000 gallons bed volume systems mentioned previously, a volume of 3, 750 gallons of 47. 5% sugar liquor would be obtained. Recall that under equilibrium conditions in a batch process, twice as much volume (i. e. , 7, 500 gallons) of 39% sugar liquor would be produced.

SWEETENING-OFF

When the absorptive capacity of a carbon for color has been finally depleted, recovery of the sugar before discarding or regenerating the carbon must be done, because the amount of sugar held in the pores is considerable. This is true for both powdered and granular forms of a given carbon, because their particle size is independent of the porosity. Also, obviously, sugar liquor is in the void spaces between particles and must be recovered. Based on typical values of 0. 85 to 3. 0 ml. /g. on the porosity of carbon, the amount of sugar solids that must be recovered from the pores of carbon can range from 0. 06 to 2. 3 lb. /lb. of carbon.

The time dependency of the removal of sugar from powdered carbon cake upon water washing is shown in Figure 5. The data pertinent to Figure 5 is given in Table 2. Note that the carbons differ in porosity. For carbon A, the value is 1. 0 ml. /g. and for carbon B, 2. 6 ml. /g. In terms of diffusion theory (11), the system is considered to be the diffusion of material from a small volume into

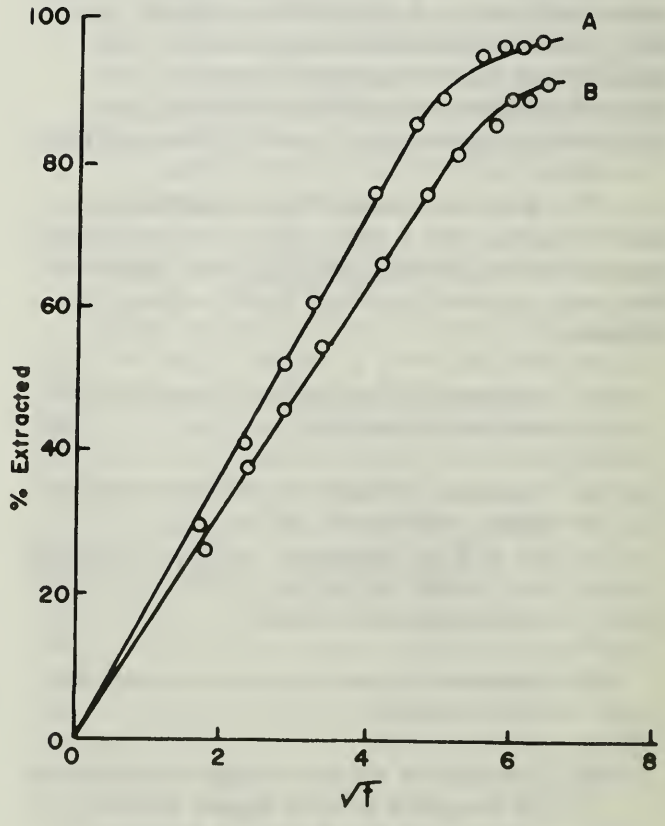

Figure 5. Extraction of Sugar from Powdered Carbons
Wash rate = 3. 6 gal. /(sq. ft.)(hr.)
Cake thickness = 1/2 inch

Table 2. --Data Pertinent to Extraction of Sugar from Powdered Carbons Illustrated in Figure 5

Carbons	Porosity, ml./g.	Particle Radius, microns	Weight of Cake, g.	Void Volume of Cake, ml.
A	1.0	40	7.15	6.4
B	2.6	40	3.85	6.4

a considerably larger volume. A simplified form of the relations of this type of system is given in equation 4.

$$E = \frac{D^{1/2} t^{1/2}}{(V + WP)R}. \qquad (4)$$

Where:

E = % extracted,
t = time,
D = diffusion coefficient,
V = void volume of cake,
W = weight of carbon,
P = porosity per unit weight
R = particle radius.

Void volume is included in the relation because the distances between particles in the cake of powdered carbon are small enough to be considered as large pores.

The curves in Figure 5 illustrate that carbon A is sweetened off faster than carbon B. Also, when they have been washed an equal amount of time to remove most of the sugar, more will remain in carbon B than A.

Unfortunately, data were not available on carbons of different access pore size to illustrate the relation of the effective diffusion coefficient to the radius of these pores. Presumably, the relationship that was shown for the adsorption of color would apply as well to the diffusion of sugar out of carbon pores.

In the recovery of sugar from granular beds, diffusion control creates the problem of obtaining good sugar recovery while trying to minimize the amount of dilute liquor. Intuitively, it can be recognized that low flow rates will achieve the best results. This is evident when the extraction is considered under equilibrium conditions, as shown in Figure 6. The data are for the typical case

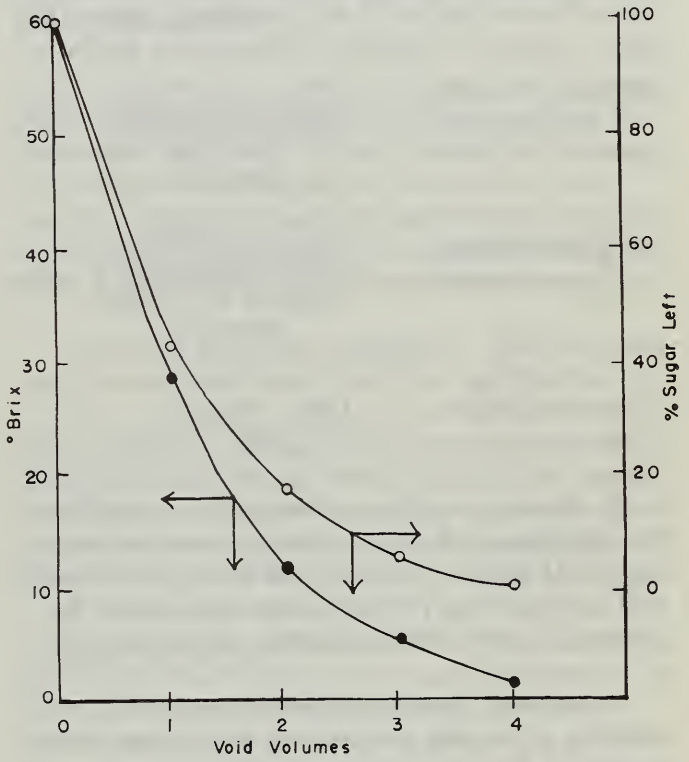

Figure 6. Equilibrium Sweetening-Off of Carbon by Decantation

of a carbon with the density of 24 lb./cu. ft. and 50% void volume. The washing is done by adding sufficient water to fill the void volume. When equilibrium is achieved, this water is decanted and another volume added. The results are shown as the concentration of sugar liquor in the liquid phase and the percentage of sugar solids remaining in the carbon. Note that with four decantations,

the Brix drops from 60° to about 2°, while the percentage sugar left falls to less than 1%. Experience in a number of refineries has shown that this equilibrium washing is closely approached at flow rates less than 0.1 bed volume per hour.

REGENERATION

Since adsorption takes place within pores, and carbon particles are rigid, i.e., they do not change volume upon adsorption, the measurement of particle density of spent carbon compared to its virgin counterpart can be used to obtain the amount of sorbed impurities along with any residual sugar that may remain. This is illustrated as follows:

$$\text{Particle Density of Virgin Carbon} = \frac{\text{Weight of Carbon}}{\text{Volume of Carbon Particle}} = Dv$$

$$\text{Particle Density of Spent Carbon} = \frac{\text{Wt. of Carbon + Sorbed Impurities}}{\text{Volume of Carbon Particle}} = Ds$$

$$\%\ \text{Sorbed Impurities} = \frac{(Ds - Dv)100}{Ds}$$

Such measurements can be useful in judging the efficiency of the carbon in determining how well sugar removal has been carried out, and in adjusting regeneration conditions for unusually low or high loading of the carbon.

Particle density measurements can be done by a simple procedure and literature is available for conducting these measurements.* For most granular carbons available today, the particle density can be related directly to porosity without making the more complicated measurement of skeletal density of 2.0 ± 0.05 g./ml. In the regeneration of granular carbon, it is necessary to restore the original porosity in order to achieve a restoration of the original adsorptive capacity. Thus, particle density is a simple effective method for establishing proper regeneration of granular carbon. This was the subject of an earlier paper presented at the previous technical meeting of this group (1).

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SUMMARY

The porosity of activated carbon has been presented in terms of total pore volume and the distribution of pore volume according to pore size.

The porosity of activated carbon establishes a diffusion barrier which in turn dictates the time dependency of adsorption. Furthermore, it dictates the time dependency of the diffusion of sucrose into and out of carbon. At present, the relationships for the time dependencies of these processes, based on diffusion models, are well established for batch systems. However, further work is necessary in establishing relationships for flow through a granular bed.

Finally, particle density can be used as an effective method to establish the restoration of porosity upon regeneration of granular carbon.

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DISCUSSION

R. S. Joyce (Pittsburgh): In the second equation that you showed for the rate of adsorption in a fixed bed, you had a factor defined as porosity; in what units would this be expressed?

J. T. Truemper (Atlas): Porosity would be in ml./g. Essentially what you have to determine in the system is the porosity of the dosage where you have ml./g. of carbon times the dosage of the carbon, and this really gives you the total pore volume into which you are diffusing.

R. S. Joyce: You implied that the degree of surface covered would be governed by spatial consideration and by the oxide content of carbon surface. Would you care to elaborate on how the oxide content governs the surface coverage?

J. T. Truemper: It has been observed that with varying oxides on the carbon you get different adsorption of color species from sugar solutions. It is not constant from one system to the next; these are not really clear data, but we can recognize that there can be an effect. What's more obvious about the phenomenon can be seen in studies of pure compound adsorption. One of the effects observed in our work was the competition for oxide sites by water and the materials being adsorbed. We found that acidic materials were less successful in the competition than basic material so, by extending these concepts, we feel that this does have an effect and that the surface area can not be used as a guide to efficiency of adsorption of something like color from sugar.

K. R. Hanson (American): These carbons all have a certain amount of irreversibly adsorbed sucrose. Is there any chance of altering the manufacture of these carbons to reduce this irreversibly adsorbed sucrose, while still not affecting the decolorizing ability of the carbons?

J. T. Truemper: I feel that perhaps by alteration of the oxides you might change this retaining of sucrose. I don't think that we want to change the structure of the carbon too much. Most carbons are pretty well proven as good adsorbents and we wouldn't know what a structure change might do to us.

Let me ask you a question. Do you have any idea of how much sucrose is adsorbed?

K. R. Hanson: Frank Carpenter reported sucrose adsorbed on bone char and we duplicated his work; these granular carbons of course sweeten off much more slowly, but what the sugar retention is, I could not say.

J. T. Truemper: I believe there is some confusion about data of sucrose adsorption on these granular carbons because of this diffusion process. It always raises a question of have you really gone long enough in the sweetening off. Was that sucrose really irreversibly adsorbed? Or did you just not sweeten off enough?

E. D. Gillette (Refined Syrups): Could you make your carbon more specific for certain color bodies by adjusting the pore size distribution in regeneration?

J. T. Truemper: We have made overactivation studies. We find that there is no specificity of attack on carbon by steam or a small

amount of oxygen, and all pores are increased to about the same extent, so we cannot adjust pore size distribution. It has been the desire of a lot of researchers in academic circles to make activated carbons that are molecular sieves, and they try to do this by taking a well ordered polymeric material and charring it. They have had some success, but when you are dealing with a practical commercial process, you are talking about a raw material of a less crystalline order, like coal or lignite. This makes a certain kind of pore distribution, controlled more by the raw material, and only a little by process. To give one good example - generally, you make gas carbons out of different raw materials than decolorizing carbons.

E. D. Gillette: I have heard it inferred here today that, with continued use of liquors over carbon, you may displace this sucrose which has been adsorbed in the early part of the cycle. If this is true, would not this also mean that other nonsucrose constituents of liquors might be displaced from the carbon further along the cycle?

J. T. Truemper: Yes, this is quite likely. Of course, we are talking about quite a soup, but sometimes I think that what we consider lack of adsorption could very well be considered as a displacement by something else that is more preferentially adsorbed. All we ever see are grand averages when we just measure color. There are a number of mechanisms that could be operating. This is why I am trying to shoot down any judgement of adsorptive efficiency based on surface area.

SECOND SESSION: Fred Bruder, SuCrest Corp., Chairman

REVIEW OF SUGAR ORIENTED ION EXCHANGE PRACTICES

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Cicero, Ill.

INTRODUCTION

The references cited in this paper cover a 26-year span. They are by no means exhaustive, but are believed to be representative. In addition to a review of the references, some thoughts will be given on future potential of ion exchange, both process-wise and equipment-wise.

This paper falls generally into four sections. First, a discussion of single resin systems, cation or anion; second, a discussion of multiple resin systems; third, a discussion of newer equipment techniques; fourth, a discussion of possible combinations of new process and new equipment.

One of the earliest mentions of ion exchange materials in the sugar industry was by Harn in 1896. He suggested that natural zeolites could be used for replacing the melassigenic alkali metal cations for the less melassigenic calcium cations to improve sugar yield. He was granted a German patent, #95447, on a process involving this, in June 1896. In the proceedings of the Verein Deutcher Zucker Industries of 1903, Volume #53, page 798, a Mr. A. Z. Rumpler reports conducting experiments using cation exchange in the beet industry. In 1907, in the same journal, Mr. A. Z. Gans, Volume #57, page 931, suggested the use of synthetic zeolites instead of natural occurring zeolites, in order to increase the degree of exchange reaction.

In 1935, Adams and Holmes developed and patented the production of ion exchange materials from the sulphonation of organic materials, and synthetic anion and cation exchange resins came into being as a commercial product. Their production was covered by U. S. patent 2,104,501, which was issued January 4, 1938.

In 1936, Liebknecht suggested for the first time that demineralization of sugar solutions, by the passage successively through an acid regenerated cation and an alkali regenerated anion, could be achieved. Liebknecht was issued French patent, 808612 in 1936 and a corresponding U. S. patent 215,318 in 1939. Shortly after this time (1939), references to the use, or the possible use, of ion exchange in conjunction with the sugar process begin to appear in greater frequency and it is at this point that the references shall be selectively classified.

SINGLE RESIN SYSTEMS

Single resin systems fall first into the categories of cation or anion. The cation section may further be sub-divided into the use of single cation systems in the process which is to be accomplished, namely: softening, cation substitution, inversion, and ion exclusion, and the anion single resin systems can be subclassified to decolorization and anion substitution.

Softening is generally applied to thin juices to prevent or at least minimize evaporator boil-outs due to lime salt scaling. The process is simply the matter of passing the filtered thin juice or raw juice over a bed of cation exchange resin in the sodium form to exchange calcium and magnesium for sodium. Regeneration is accomplished with sodium chloride solution, with 12% being the most commonly used concentration of regenerant. Installations have been reported with fixed bed, utilizing both co-current and counter-current regeneration, continuous indexing fixed bed, and continuous counterflow moving

bed equipment (See table 1). The majority of the installations reported are fixed bed co-current regeneration.

Juice softening is widely practiced in the European beet industry. The economics seem to be better there than they are in the United States, principally because lime salts are higher in European beet juices. Several applications (though not very many), have been reported in the cane sugar industry throughout the world. One typical reference (1) to the beet sugar industry reported lime salt reduction of 50% and reduction in boil-outs during campaign to 50%. The same reference reported an additional benefit from softening, which has not generally been reported--that is the elimination of necessity to re-melt strikes during campaign, due to turbidity. Another beet sugar reference (2) cites lime salt reduction of 60% and boil-out reduction of 67% with the effect that campaign length was decreased by 7 days. One cane sugar reference (29) indicates that the same could be true in cane sugar factories and also indicates the potential use of sea water for regeneration of the cation resin.

Cation Substitution should be distinguished from softening, because cation substitution systems are concerned with the melassigenic nature of various salts (table 2). Two such processes that have been utilized commercially are quite opposite in application, but still operate under the same premise.

Diagram 1 shows the two processes schematically. In the SCC process (5), filtered beet thin juice passes over cation resin in the ammonium form, converting the ash represented by sodium chloride to ammonium chloride. This juice is treated with an excess of lime and then neutralized with CO_2 in what might be considered a third carbonatation step. The resultant juice is filtered to remove the precipitated calcium carbonate and the ammonia is driven off during the evaporation step. The result is that the mineral matter is reduced, and in addition that remaining is mostly calcium salts which are far less melassigenic than sodium or potassium. It is claimed that final molasses purity can be reduced from 58% to 45%.

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Table 1. --Softening

Purpose	Method	Point of Application	Flow Rate gpm/ft.^{2}	Regenerants Used	Comments & References
Exchange of hardness for sodium	Cation exchange polystyrene divinyl benzene resin 8% cross linked	Thin Juice Beet	6-8	NaCl 12%	Widely practiced European Beet Sugar Factories salts usually higher than in U. S. A. eliminates scale in Evaporator
	1. Down Flow Fixed Bed	Raw Juice Cane	6-8	NaCl 12%	Application in raw cane factories usually also req. filtration.
		Thin Juice Carb. Fact.	6-8	NaCl 14%	Good efficiency data
	2. Continuous indexing fixed bed	Thin Juice	6-8	NaCl 12%	Aconex - applied Eridania Sugar - Italy, 1963. Also reported France 1967
	3. Continuous counterflow moving bed	Thin Juice Beet	30	NaCl 12%	Sugar Mill at Vic s/Aisne Sugar Mill at Cagny Sugar Mill at Arcis s/Aube

Table 2. --Cation Substitution

Purpose	Method	Point of Application	Flow Rate gpm/ft. ^{2}	Regenerants used	Comments & Reference
Exchange Melassigenic Nature of Feed	Cation resin to replace Na and K	2nd Carb. Juice	6-8	$(NH_4)_2SO_4$ +CaO	Leopoldsdorf Factory, Austria 1958 "SCC" Process Molasses purity drop from 58 to 45%. (5) Increase white sugar 0.7% on beet.
	Cation resin to replace Na and K with Mg	Intermediate-greens beet (machine syrup)	1.0	$MgCl_2$ 6%	"QUENTIN" Process fairly widely used in Germany and Austria (6) Also installed in NYSSA factory 1966 and RUPERT factory 1967 - molasses purity drop from approx. 59 to 53. (7)

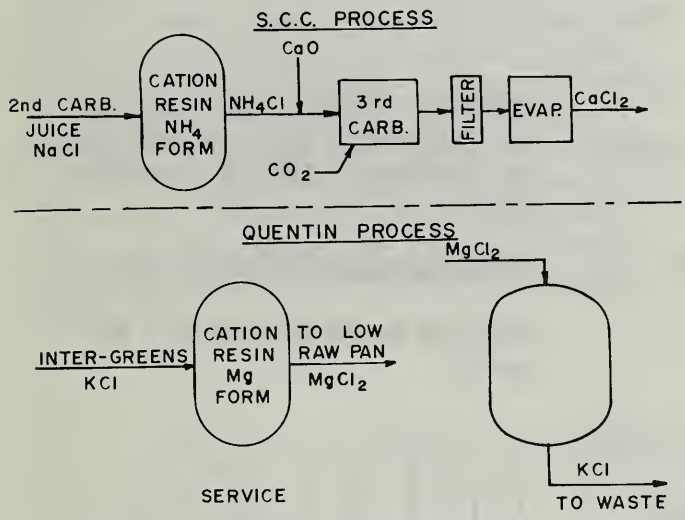

Figure 1. Cation Substitution Processes

picts in simple terms a Quentin Installation (6), several of which are in operation in the European beet industry and two of which are in operation in the United States. In this application, intermediate greens or machine syrup are passed over a strong acid cation resin in the magnesium form. Regeneration is accomplished with 6% magnesium chloride. Potassium, the principal component of the cations in the feed to the columns, is converted to magnesium, which is less melassigenic. Molasses purity can be reduced approximately 5 points in this system, and it would appear that added benefits are to be found in low raw centrifugal behavior. Although regenerant re-use is currently practiced, a study of the process and reported results indicates that quite probably a second re-use of partially exhausted magnesium chloride regenerant could be effected by running it across a macroporous anion resin to be used in a decolorizing step. Calculations indicate that waste magnesium chloride can be utilized to regenerate sufficient anion resin to remove approximately 1-1/2 Horne scale units of color, from the standard liquor flow of the same factory for which the magnesium chloride/cation station was calculated.

Table 3 gives data on Ion Exclusion. This process has the unique distinction of using water as its only regenerant. Actually sodium chloride should be listed as a regenerant as well, because the column feed is generally softened prior to ion exclusion. Ion Exclusion (8) may be described as utilizing an ion exchange resin, but not for ion exchange

Table 3. --Ion Exclusion

Purpose	Method	Point of Application	Flow Rate gpm/ft.^{2}	Regenerants used	Comments and Reference
Ash Removal	Use of Ion Exchange resin (cation because of cost), and taking advantage of tendency of non-polar pure sugar solution to enter pores of resin first. 4% cross-linkage	30-40° Bx. Juice Beet	1/2	Water (NaCl)	Juice must be softened first; hi-dilution, 50% impurity removal, hi-sugar loss. (8) Continuous equipment deemed necessary.
		Beet Molasses diluted to 40°	1/2	Water H_2SO_4 10% NaOH 5%	Assalini "B" Process (9) same general comments as above. Diluted molasses split to 2 streams; one over partially regenerated anion; other over partially regenerated cation; effluents are blended. (10)
		Cane "B" molasses diluted to 40° Bx.	1/2	Water	U. S. Patent 3,214,293 (30)
		Softened affination syrup 60° Bx. 180° F.			Seems to revolve around use of countercurrent regn. of softening col. and use of 180° F. temperature.
		Dilute beet and cane molasses 90° C. 40° Bx.		Waste	No performance at 25° C. (35) Estimate could achieve 80 - 90 purity.

purposes. A conventional strong acid cation resin may be employed, but the percent divinyl benzene cross-linkage is controlled to four and in some cases three percent (32). Control of the cross-linkage affects the chemical/physical properties of the resin to permit a faster diffusion of the pure sugar solution into the pores of the resin bead.

The sugar molecules enter the pores of the resin beads, which are actually quite porous, while the color bodies are physically too large to enter and, therefore, are excluded.

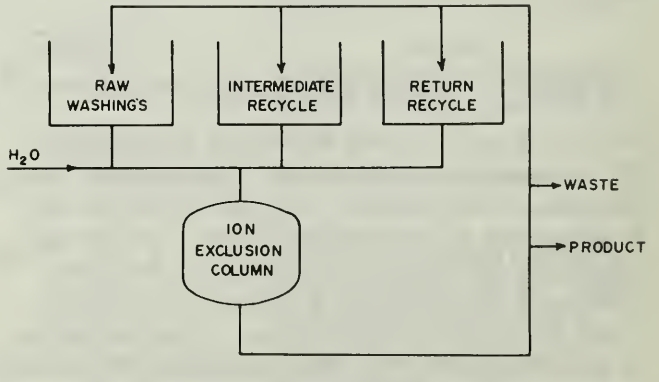

Diagram 2. Ion Exclusion Process

A phenomenon called the Donnan membrane effect also causes ionizable compounds to be excluded from the pores. The sugar itself would be somewhat equally distributed inside and outside of the bead, perhaps even at higher concentration inside due to adsorption. The result is that the solution inside the bead is relatively pure sugar, while most of the impurities are outside the bead. Elution with water produces several fractions which are selectively collected or discarded (9, 10). Diagram 2 gives the general flow scheme for Ion Exclusion equipment. Additional comments will be made on the potential for the Ion Exclusion process at the end of this paper.

Table 4 shows cation inversion. Sucrose at approximately 65° Brix is run across cation resin in the hydrogen form, which resin acts as a catalyst for the inversion of the sucrose. Tests (28) have indicated that sulfonic resins are more effective than carboxylic resins, and further that rates increase with a decrease in the particle size of the resin and with an increase in porosity of the resin beads. The rate determining step is the diffusion into the resin particle. Although the use of continuous equipment has not been reported in conjunction with cation inversion, it would appear that this would be an excellent spot for application of continuous equipment.

Diagram 3 shows the typical equipment used for single systems. Service steps are almost always downflow. Regeneration in units in operation at present is largely downflow (co-current), but recent references indicate a much stronger case for upflow regeneration (countercurrent), both from the standpoint of minimizing leakage and from the standpoint of reducing regenerant consumption (31).

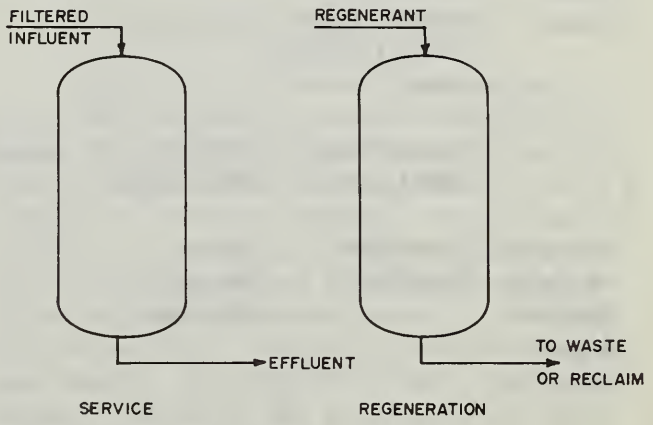

Diagram 3. Equipment for One Resin Systems
The type of underdrain system used can cause up to 100% variation in quantity of sweetwater produced

Table 5 shows anion resin decolorization. Generally, strongly basic anion resins are employed for this application, although work with weak and intermediate base resins has also been performed.

Table 4. --Inversion

Purpose	Method	Point of Application	Flow Rate gpm/ft.^{2}	Regenerants Used	Comments and Reference
Inversion of Sucrose	Cation resin hydrogen cycle down flow fixed bed.	65° Bx. Sugar 25, 50, 75, 88, 100° C.	1	4% H_2SO_4	Sulfonic more effective than carboxylic - rates increased with decr. particle size and incr. porosity. Rate determ. step is diffusion rate into resin particle. (28) Probably good application for continuous flow.

Table 5. --Decolorization

Purpose	Method	Point of Application	Exh. Rate gpm/ft.^{2}	Regenerants used	Comments and Reference
Removal of Color Bodies from Sugar	Anion resin adsorption Micro and/ or Macro-porous type resin (strong base).	Beet thin Juice	6-8	NaCl 12%	Aomori Factory 1962 (4). Hombetsu Factory 1963. Split stream - approx. 25% total juice
	Down flow fixed bed	Beet re-melt sugar	1-1/2 -2	NaCl 12%	Same factories - total remelt flow average 67-70% color removal
Removal of Color Bodies from Sugar	Down flow fixed bed	Cane Liquor off-char	2	NaCl plus HCl occ. 0.2 lb./ CF/ cycle	NaOCl treatment of resin may be necessary periodically. Colonial Sugars - Gramercy, La. 1966. 2,250 Horne gals. per CF cycle IRA 900 (22). Columns designed for multiple service.
Removal of Color Bodies from Sugar	Down flow fixed bed	Cane Liquor off gran. carb.	1-1/2	NaCl plus occ. NaOCl	Southdown Sugar, Houma, La. 1964 2000 Horne gal. per CF per cycle 401S replaced by 900 - No significant difference. Columns designed for multiple service.
Removal of Color Bodies from Sugar	Down flow fixed bed	Cane liquor carb. plant		NaCl 12%	Drop in efficiency due to organics fouling can be controlled with HCl and NaOCl (25)
Removal of Color Bodies from Sugar w/ high surface area.	Powdered anion resin coated and kieselguhr	Cane liquor 40° Bx.		Not indicated	80-90% color removal. No performance at 55° Bx. (34)

Several references for applications in both cane and beet sugar are available. The system is quite analogous to softening since regeneration is again accomplished with sodium chloride brine. This is not, however, a true ion exchange process since decolorizing continues after the exchange capacity of the resin has been exhausted. Most of the

references will cite a necessity for a periodic clean up of the resin with sodium hypochlorite solution. The purpose is to elute some of the organics not removed by simple brining. Our own experience has been that the use of sodium hypochlorite can be relatively ineffective and often a mineral acid such as hydrochloric should be used.

Very little data are given in the literature or by manufacturers on absolute capacity of anion resin for decolorization. With the cooperation of some users of anion decolorization, data have been kept which indicate that the capacity of anion resin for decolorization is approximately equivalent to 2000 to 2250 Horne units per cubic foot per cycle. On initial cycles, capacities are probably somewhat higher, but this would seem to be a good average figure, over the life of the resin. With periodic acid treatment, resin life might be expected to be as long as two years in continuous use.

Anion substitution is covered by Table 6. In this application, strongly basic anion resin in the hydroxide form is used to convert anions to a form that will floc with selected cations in the form of water soluble metal salts. One purpose reported from the beet sugar industry is to eliminate the normal carbonatation steps. Beet juice off the anion substitution column is subjected to a treatment involving the addition of calcium sulphate or calcium chloride to produce a precipitate which is subsequently filtered out. The process has been reported (23) as suitable for application with raw juice or partially demineralized molasses.

MULTIPLE RESIN SYSTEMS

Table 7 shows several references to two-resin systems aimed at non-sugars removal (Demineralization). Some of the first studies explored the relative efficiencies of 2 column vs 4 column systems, regenerant reuse, and prevention of fouling. But the use of ion exchange proved uneconomic because of: increasing regenerant costs, increasing molasses prices, relatively inefficient equipment design, and relatively short resin life. Happily, the latter two problems have been greatly improved upon.

Work at Burley, Idaho (11), averaged 72% ash removal, but at a loss of Brix and increased invert. It became quite apparent that

Table 6. --Anion Substitutions

Purpose	Method	Point of Application	Regenerants used	Comments and Reference
Convert anions to form that will floc with selected cations in form of water sol. metal salts (Al, Fe, Mn) eliminate carb. steps	Anion resin to replace SO_4, CO_3, etc. with OH followed by treat with $CaSO_4$ .3% in juice and filtration	Raw juice beet or partially dil. molasses	NaOH	Assalini "A" Process (23) not commercially applied to date. U. S. Patent 2,929,746 Anion subs. and filter followed by anion (401S) and weak acid cation (IRC 50) to avoid regenerant in high quality sugar. Excess caustic from this step sent to anion substitution station for regeneration.

Table 7. --Demineralization

Purpose	Method	Point of Application	Flow Rate gpm/ft. ^{2}	Regenerants used	Comments and Reference
De-ashing	Cation-Anion	15° Bx. filtered juice 20° C. Beet		$H_2SO_4 + Na_2CO_3$	Amalgamated Sugar Burley, Idaho (11) 1941-42; 72% ash removal, some inversion (12)
		15° Bx. filtered juice 20° C.		$H_2SO_4 + Na_2CO_3$	Layton Sugar Co., Layton, Idaho (13) 1946
		15° Bx. filtered juice 20° C. Beet		H_2SO_4 + NaOH	Alvarado Factory Holly Sugar (14) 1946
		15° Bx. filtered juice 20° C. Beet		$H_2SO_4 + NH_4OH$	Hardin Factory, Holly Sugar 1947. (15) Higher than estimated operating cost, poor water supply; lower efficiencies than expected.
	Cation-Anion	15° Bx. filtered juice. Beet		$H_2SO_4 + NH_4OH$	Amalgamated Sugar. Twin Falls - '50-'51. 95.4% ash removal. (16)
	Cation-Anion	Middle juice beet (45° Bx.) 14° C.		HCl + NaOH	0.7% sugar on beet recovery, high water consumption. 1965 (18)
	Cation-Anion Anion	15° Bx. Juice beet 11° C. 80% of flow		H_2SO_4 + NaOH	Double anion to increase resin efficiency and remove more color. Hombetsu Factory, 1963 (4)
	Cation-Anion Anion	30° Bx. 80° Pure beet juice and #2 green		6% NH_4OH 10% H_2SO_4	60% non-sugar elimination counterflow regn. re-use. (31)
	Anion-Cation Anion	Cane clarified juice 15° Bx. 70° F.		H_2SO_4 + NaOH	Anion scavenger removes nitrogenous compounds est. 8.3% incr. in removable suc. (36)
	Mixed Bed	60° Bx. syrup 125° F. Cane	1	H_2SO_4 + NaOH	Report on East Coast Cane Refinery (17)

inversion due to the catalytic effect of cation resin was much greater than that due to low pH alone.

Rawlings and Shafar (12), reported 60% - 70% removal of non-sugars, 95% removal of ash, and 30%-50% removal of organics. Regenerant consumption was 11 lbs. 93% acid and 12 lbs. soda ash per ton of beets. In addition, 80% - 90% of the ultra-microscopic colloids were removed - an unexpected bonus.

The work at Layton (13) indicated that molasses production could be reduced to only 20% of former production for the factory. At Alvarado (14), two two-bed units were operated in series thus increasing removal of non-sugars to 87%. The work at Hardin (15) proved not to be economical at the time due to greatly increased regenerant prices and simultaneously increased prices for molasses.

Cane refineries (17) probably made deionzation "stick" at an earlier date. The lower ash levels "on" made it feasible to use Ion Exchange as a polishing tool for the producing of liquid sugar. Studies were also made on the use of Ion Exchange for treatment of cane juices, (26, 27, 36, 37). Various regeneration systems were explored but generally speaking successful systems used acid and caustic. Cane refineries have also used fixed bed, mixed bed deionizers for some years, chiefly in conjunction with low ash liquid sugar production.

Fixed-bed, mixed-beds are known to give better quality and less inversion, but they are more expensive to operate because of poorer regeneration efficiencies.

The next series of diagrams illustrates some of the two resin methods used for demineralization and points out advantages and disadvantages for each.

Diagram 4 shows two-bed demineralizers for ash removal, operating in series to increase effluent quality. The two-bed unit on the right is being regenerated and the regenerant may be applied downflow (solid lines) or upflow (dotted lines). Upflow regeneration has the advantage of most completely regenerating the resin at the bottom of the bed so that in service, the liquor contacts the "best" resin just before leaving the system. This too tends to increase quality. However, upflow regeneration introduces the possibility of resin-bed expansion and resin-loss, so most installations employ downflow regeneration.

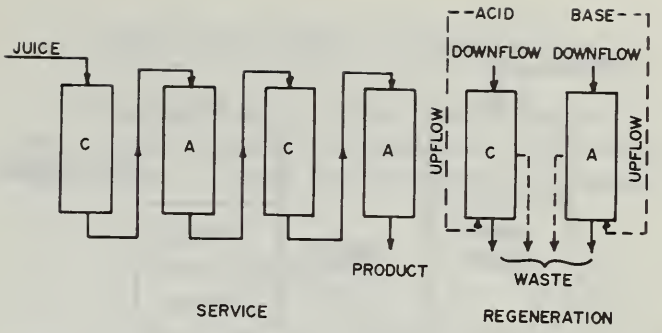

Diagram 4. Two Bed Deionization

Another problem with two-beds is the degree of inversion. The cation resin can be considered a solid mineral acid and passing through a cation column promotes inversion. Some of this problem is overcome by reverse deionization in which the flow is first through an anion exchanger and then through the cation exchanger. Thus the pH is first raised quite high and then brought back down by the cation. In this way, less inversion is encountered. However, in reverse deionization it is necessary to use a strong base anion resin so that neutral salts are split to allow deionization. These have much poorer economics than the weak base resins which can be used in conventional (cation first) deionization. In addition, reverse deionization contacts the anion resin with the juice just as it enters the process. In a conventional system, there is some, "clean-up" by the cation resin before flow reaches the anion. Since anion exchangers are quite susceptible to organic fouling, this is an important consideration.

Diagram 5 shows a conventional mixed-bed regenerated in place. Higher quality is attained and inversion minimized because there is no contact with cation resin alone.

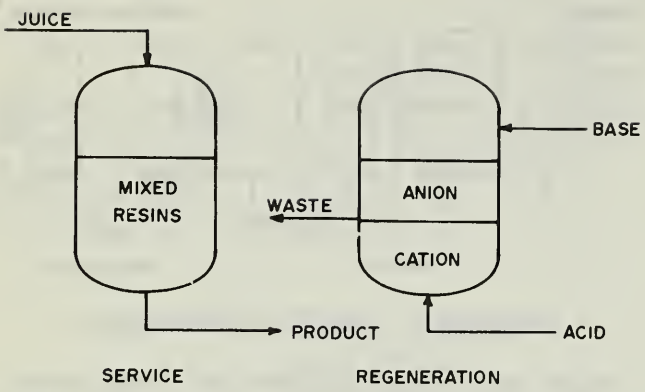

Diagram 5. Mixed Bed Deionization
Fixed Bed Operation

The resins are separated by backwashing for regeneration, the wastes being collected from a distributor at the interface of the resins. However, the resins swell and shrink and their interface seldom occurs at the interface distributor. Consequently, acid contacts anion resin, or caustic contacts cation resin, and there occurs a band of resin at this interface which is never regenerated. Thus the efficiency of a mixed-bed is reduced.

Diagram 6 shows an externally regenerated mixed-bed system. Here an exhausted, mixed-package of resin is transferred, in

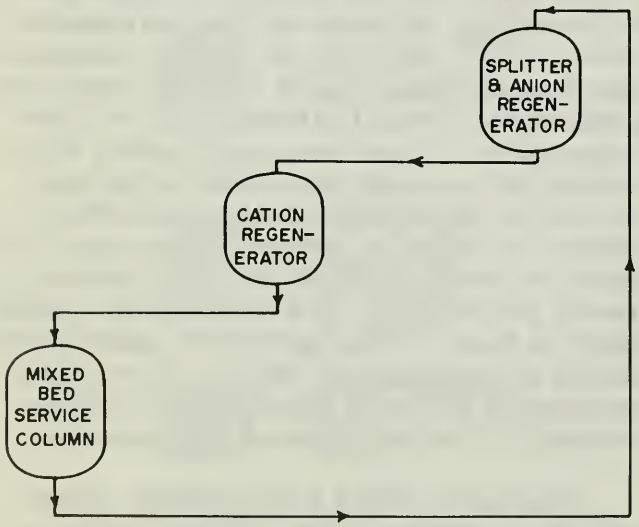

Diagram 6. Externally Regenerated
Mixed Bed

juice, to the splitter column where enough water is added to drop the specific gravity of the juice to 1.2. At this density, the anion resin floats and the cation sinks leaving a band of liquor between. The cation is dropped to the middle column, and both resins are sweetened-off and regenerated in their separate columns with the efficiency of a two-bed unit. Upon completion of the regeneration, the anion is dropped to the middle column and mixed with the cation. As soon as another service column exhausts, its resin is removed to the splitter and the newly regenerated resin replaces it. Thus, an extra package of resin is in the system, and the service columns are off stream for short periods only.

Ion Substitution, (See Table 8) may be described as a method for indirect ash removal. Consider an installation (22) of mixed cation and anion resin treating bone char effluent in a cane refinery producing white sugar. The resins are not separated for regeneration, but merely contacted with brine. Thus the cation is converted to the sodium form and the anion to the chloride form. In service, all calcium and magnesium associated ash is converted to sodium chloride, greatly increasing the solubility. Thus ash is less likely to be included in the crystal and more likely to be spun off in the centrifugals. In addition, scaling is minimized in the evaporator and color removal is accomplished; depending on the raws being melted, ash removal can be 50%.

Some equations describing another form of ion substitution, the interesting Vajna Process (19) are as follows:

A. Cation Regeneration
$2\,Rc\text{-}Na + (NH_4)_2\,CO_3 \longrightarrow 2\,RcNH_4 + Na_2CO_3$

B. Residue Treatment
$Na_2CO_3 + CaO + H_2O \longrightarrow 2\,NaOH + CaCO_3$

C. Anion Regeneration
$Ra\text{-}Cl + NaOH \longrightarrow Ra\text{-}OH + NaCl$

D. Cation Exchange
$RcNH_4 + NaCl \longrightarrow RcNa + NH_4Cl$

E. Anion Exchange
$RaOH + NH_4Cl \longrightarrow RaCl + NH_4OH$

This is a conventional two-bed process. The cation exchanger is in the NH_4 form and the anion exchanger in the OH form. Assuming the ash to be NaCl, line "A" shows the cation regeneration with $(NH_4)_2\ CO_3$. The effluent contains excess regenerant plus Na_2CO_3; this is evaporated to recover the NH_3 and the residue treated as in line "B" with lime, giving NaOH and $CaCO_3$. The $CaCO_3$ is removed by filtration and the NaOH regenerates the anion exchanger as in line "C". Now, in service, the juice passes over the cation exchanger giving the ash the form of NH_4Cl, as in line "D". This goes to anion exchange, line "E", yielding the ash as NH_4OH in the juice. Upon evaporation, the NH_3 is driven off giving 80% ash removal. The NH_3 is treated with CO_2 from the limestone kiln to give the $(NH_4)_2\ CO_3$ for cation regeneration. Thus only CaO is utilized for regeneration chemicals.

NEW EQUIPMENT TECHNIQUES

Diagram 7 shows what will be the next step - continuous ion exchange on a de-ashing application. Three such schemes are shown

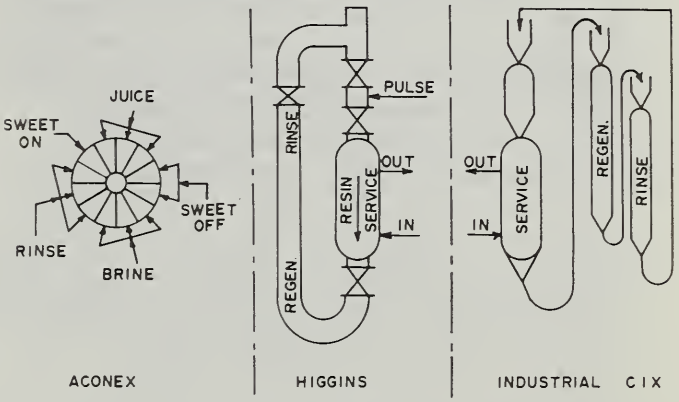

Diagram 7. Continuous Contact Systems

here in very simplified form. The Aconex (3) unit has compartments which rotate into different zones. The Higgins unit has the resin moving into various zones of a closed loop carried along by a flow of liquid. The

Table 8. --Ion Substitution

Purpose	Method	Point of Application	Flow Rate gpm/ft.^{2}	Regenerants used	Comments and Reference
Reduce ash on crystal	Mixed Bed	Cane Liquor off Gran. Carb. 60-65° Bx. 160-180° F.	1.5	NaCl 12%	Reduce ash on crystal approx. 50%.
Reduce pan scale					Remove approx. 0.3 units Horne color.
Decolorize					Southdown Sugars - Louisiana (22)
Reduce Ash	Cation + Anion	Clarified Cane Juice - 70° F.		$(NH_4)_2SO_4$ NaOH	Convert ash to NH_4OH flashes in evaps. (26, 27)
Reduce Ash	Cation + Anion	15° Bx. Juice Beet - 100° F.		CaO	Equipment not usually found in sugar factory (19)

Industrial CIX unit moves the resin into different columns for the various processing steps. The motive force is air pressure.

During the earlier course of the paper there were two references in the softening table, (Table 1), to continuous operating equipment. One was a fixed-bed unit and the other was a moving-bed unit. Both were operating on softening service on beet sugar juices. Throughout all of the tables, on different systems a number of operating problems were noted. Because of the fact that regeneration efficiency, cost of regenerants, and exhaustion efficiency indicated by quality of effluent seemed to be the central theme of the problem, it is believed that this continuous concept should give many of the answers to those problems raised.

Returning again to Diagram 7, and examining it in more detail, it is quite true that there are more continuous systems on the market than those illustrated, but those three best illustrate the points to be made. The Aconex contactor of Italy is a fixed multicellular indexing type of contactor. Regeneration and exhaustion are counter-current to resin movement. Resin movement is accomplished by allowing a certain portion of the influent flow to "slip" and pull the resin to its next position in the loop. Regeneration is accomplished by pumping the regenerant through the resin in the regenerant section.

Industrial's CIX system is a moving-bed pulsing loop type contactor. Regeneration and exhaustion are counter-current to resin movement. Resin movement is accomplished by allowing the resin to fall into a column of regenerant, which is flowing counter-current and upward due to differences in hydrostatic head. All of these concepts have relative merit. Because of their continuous, or almost continuous operation, they offer the sugar manufacturer the possibility of avoiding "on" and "off" stream loads on other parts of the plant. They should also offer the possibility of closer process control on each of the sections of the continuous unit (which corresponds to the cycle steps of a non-continuous unit), and consequently more efficient regenerant consumption, and better sweetwater management.

NEW PROCESSES

Resins are now available which greatly enhance the feasibility of continuous equipment for sugar processing. The macroporous resins are much more resistant to fouling and higher cross-linked materials are better resistant to osmotic shock. Many new resins exhibit the low attrition losses necessary for moving bed operations. A further look at each continuous unit is in order. What is the best probable use for each in the sugar industry? Since there are more Higgins Loops operating in the United States than any other type of continuous contactor, let us consider the Higgins Loop first. As stated before, regeneration and exhaustion are counter-current to resin flow. Therefore, effluent quality, exhaustion efficiency, regeneration efficiency, and regenerant consumption should all be extremely favorable. With the new resins available, attrition losses should be moderate (say 10 to 20% per year). What feed stream should be treated? Resin is moved from station to station by slip. If sugar solution is used, a fairly large quantity of sugar solution will pass into the de-sugaring section, resulting in a relatively large quantity of sweetwater. Certainly sweetwater can be handled and "worked" into other phases in the refinery, or even in preparation for the deionizing step itself.

Alternately, if this system is used on plant water intake, for example, all of the exhaustion and regeneration efficiency cited earlier should still apply, and the disadvantages inherent in the use of "slip" as a method of resin movement, would not affect the sugar stream.

Since the two systems are somewhat similar, let us next examine the CIX type system. As stated before, regeneration and exhaustion are counter-current to resin flow; therefore, the same comments should apply concerning effluent quality, exhaustion

efficiency, regeneration efficiency, and regenerant consumption as applied to the system discussed first.

It may be that the free-falling regenerative system with CIX could give a little better regenerative efficiency, but this is a problematical point at this stage.

Considering the method of resin movement, namely, the application of pressure from external gases, slip in the system is virtually zero (in the magnitude of 1 of 2% as opposed to 25% or 30%). Based on these considerations, it would appear that such a system should be suitable for use on either a sugar-bearing stream or water stream.

As we pointed out, regeneration and exhaustion on the fixed-bed are co-current and downflow. In observations made on the tables presented earlier, it would appear at first blush that such a system, which, for example, doesn't allow for counter-current regeneration, must lose out in the process economic calculations. Regeneration efficiency, by reasoning, should be less favorable than that of the two systems considered earlier. This, of course, is pre-supposing the use of acid and/or alkali for regeneration, or perhaps we should say, instead, this is pre-supposing the use of resins for ion exchange.

Alternately though, if the resins are considered as being used for ion exclusion, none of the data available indicate that counter-current regeneration (with water), gives any greater efficiency. Data indicate, however, that fixed relationships between the various fractions in the steps of the ion exclusion process are extremely beneficial. It would appear that a multi-cellular indexing type system would lend this type of fixed relationship, and therefore, it would seem that the best possible spot to apply such a system would be to the problem of Ion Exclusion. This is not to say that the other two systems considered would not be suitable for Ion Exclusion, but it would appear that the possible use for systems like Aconex would be for this purpose.

Whether the piping system feeding the multiple cell unit indexes, or whether the cells index under a fixed pipe system would seem to make little difference.

CONCLUSIONS MAY BE DRAWN AS FOLLOWS:

1. A good deal of time and money has been expended by the sugar industry to explore many different ways in which ion exchange can be used in conjunction with the sugar process.

2. Resin capacities and physical capabilities have changed a great deal since early work was performed and reported.

3. Equipment concepts have also changed (more recently), and it would appear that new combinations of resin and equipment applied to the proper process spots can make the use of ion exchange in the sugar process economically favorable, where perhaps it might not have been, as recently as three or four years ago.

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DISCUSSION

F. M. Williams (Pittsburgh): What were the increases in yield of refined sugar when the molasses production was reduced?

J. F. Zievers (Industrial Filters): It should be almost directly proportional; if you cut your molasses down, your yield should go up by that amount of sugar. Of course, you only have about 1/4 as much molasses as sugar and (in the beet operation) that molasses is only about 2/3 sugar, so a 10% reduction in molasses gives a 10 x 1/4 x 2/3 = 2% increase in recovered sugar.

F. M. Williams: What about the cost of this system per bag of sugar recovered?

J. F. Zievers: Unless you define the system very closely, this is a rather difficult question to answer. Rohm & Haas used to have a figure for the demineralization of water. In a 1 million gallon per day system, it was 40 cents per thousand gallons per 1000 p. p. m. However, it is hard to relate this to the cost for sugar operation as well as you have done for carbon.

G. W. Muller (Kerr-McGee): Concerning the term "slip": is that equivalent to channeling? Do you mean that in one system about 20% of the resin goes through without adsorbing for the time it should?

J. F. Zievers: No, you have that wrong. Part of the influent flow runs across the resin, another part is used to convey an exhausted portion of the resin to another position in the contacting device. That portion that is used for motive purposes is slip. A typical number might be 1000 in with 700 ahead and 300 back.

C. von Dreusch (Nichols Engineering): You mentioned a decolorizing capacity of two thousand Horne units per cubic foot of resin. Is that a Horne gallon or a Horne ton?

J. F. Zievers: That figure is stated in Horne gallons. It may be defined as the product of change in color times the total gallons through.

We have averaged some figures from fairly widely divergent sources; all the sources were operating with large size columns, and had been operating for at least a year, and even from the divergent sources the answers in terms of capacity were not over 10% apart.

C. von Dreusch: And that is for the resin most suitable for the removal of color?

J. F. Zievers: That is correct. Let me be more specific: we have compared columns using Amberlite 900 and 401S. Rohm & Haas have indicated that the 900 was superior but we really couldn't find a great deal of difference between them.

C. von Dreusch: And that is per cycle between regeneration?

J. F. Zievers: Yes.

I. M. Abrams (Diamond Shamrock): You indicated that macroporous resins are more resistant to fouling than previously available resins. Based upon information developed during the past few years, we now know that

the composition of the resin and the composition of the non-sugars in the sugar solution are far more important than porosity in determining degree of fouling. If an aromatic strong base resin is used on a syrup containing phenolic constituents, for example, the sorption is likely to be irreversible even if the resin pores are large enough to drive a truck through. On the other hand, and I think Dr. Kunin will agree with me, an aliphatic strong base resin or a weak-base adsorbent will be far more reversible with respect to the same phenolic constituents. We know also that weakly basic resins are far more reversible, with respect to the anionic color constituents present in sugar liquors, than are strong base resins. Therefore, I question the categorical implication that macroporous resins are more reversible to fouling than gel-type resins.

K. J. Parker (Tate and Lyle, Ltd.): Following the comments of Dr. Abrams, it all depends on what type of resin fouling you refer to. We recognized at least three modes: one is purely physical fouling, where the resin is fouled by particulate colloidal matter and this happens whether it is a macro reticular or gel type resin.

Other types of resin fouling are more subtle, and here I think we refer to non-regenerability, using the particular regeneration procedure which you happen to have adopted. In this connection it is quite true resins based on a styrene matrix, or those based on an aliphatic matrix, show different types of irreversible adsorption. The mechanisms are not yet understood, but there is no doubt that one of these mechanisms involves the high molecular weight fractions of color and another involves relatively low molecular weight fractions which are of relatively low anionic strength, so there are three types of irreversible adsorption, I think, to contend with. We are certainly not sure how to deal with these.

One of the methods for continuous operation of ion exchange resin process which you haven't mentioned is simply to program the flow of solutions of liquor and regenerant to a fixed system. Is there any basic objection to this type of system or is it necessary to move the resin?

J. F. Zievers: No: I am sorry, I thought we had brought that out a little better in the paper. Take the concept that you just discussed with, say, a string of 6 or 7 columns. Whether the columns or the cells move, as in the Aconex system, or whether you merely index the piping, or change the valving, should be the same thing. I can't see where there is any great difference. It is going to come down to dollars and cents for nuts and bolts. One of those answers is going to be the cheapest and that is going to be the one that will win.

K. J. Parker: Then it is purely a question of economics?

J. F. Zievers: That is the way we see it.

LABORATORY EVALUATION OF ION EXCHANGE RESINS FOR SUGAR PROCESSING

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INTRODUCTION

For purposes of evaluation, ion exchange resins fall into three categories: resins currently in service; replacement lots of resins currently in service; and resins new to the processor. The extensiveness of testing requirements varies with each category. Performances of service resins are primarily measured by the quality and throughput of a specific refinery liquor. Direct measurements on service resins, except

for factors related to attrition, are likely to be infrequent. Since replacement lots of resins currently in service have predictable chemical characteristics, measurements of physical parameters such as particle size and shape are usually of greater interest. Evaluation of a resin new to the processor requires the most extensive testing, some of it in parallel with a resin currently in service because of variations of influent liquors in the sugar industry.

Certain aspects of a laboratory testing program must be consistent with process conditions, which presumably have been determined or strongly influenced by previous pilot plant studies. This is most obviously true when a resin is evaluated for its ability to exchange ions, decolorize, or invert sucrose at an efficiency level and flow rate compatible with the entire refining process. In these latter tests criteria may vary among processors.

In this review, suggestions will be made concerning analyses of several significant properties of resins: their shapes, sizes, expansion, and contraction characteristics, color removal efficiency and deionizing ability.

SAMPLING AND PREPARATION OF A RESIN FOR ANALYSIS

In many cases a resin in service will never be sampled. Its evaluation may be completely based upon effluent quality and throughput in the refinery. In cases where a sample of service resin is required, however, the sample has a greater probabability of being representative when it is obtained between cycles after a regeneration. For replacement resins, the sample supplied by the manufacturer can be cored or the entire sample can be placed in water.

As is well known, a resin sample must be allowed to come to a full swell in water prior to conditioning or regeneration in the laboratory. A swelling time of thirty minutes is generally recommended. (If the resin is completely dry, follow the recommendations in the manufacturers' bulletins). While conditioning or regeneration in the laboratory is a necessary prelude to most analyses, its position in the testing sequence varies with the processor's particular use of the resin. For example, the processor may be more interested in the particle size of a strongly anionic resin in the hydroxide form rather than in the chloride form if the resin is to be used primarily for deionization rather than for decolorization. If the resin is supplied in the chloride form, the processor may elect to measure its moisture content in the chloride form, to see if the shipment is within specifications, and then convert the resin to the hydroxide form before measuring particle size.

Laboratory conditioning or regeneration consists of three operations: first, the resin is transferred to a column and backwashed to remove air bubbles and classify particles by size; second, the resin is subjected to two alternate treatments with dilute acid and dilute alkali; third, the resin is then converted to the desired state if such conversion is necessary for a particular analysis. For cation exchangers the sequence would be two-bed volumes each of 1N HCl - 1N NaOH - 1N HCl - 1N NaOH, with water rinses after each application; for anion exchangers the sequence would be reversed. This would effectively put cation exchangers in the sodium form and anion exchangers in the chloride form. Allowance must then be made for the fact that the weak cationic and weak anionic resins will be converted more easily to the hydrogen and hydroxide forms, respectively, than will their stronger counterparts.

SHAPE

The initial inspection of a replacement resin should include a microscopic examination of the shape of individual beads. After suitable conditioning and draining of excess water, several dozen beads should be examined on a microscope stage at a magnification of 50-100. Of interest in a new resin are the frequencies of irregularly shaped beads, split beads, and resin agglomerates.

Numerous split beads in a new resin suggest potential problems in operational systems. One should particularly examine service resins for these bead cracks, a result of stresses applied during cyclical expansions and contractions.

Clumps of resin on the microscope stage may be either flocculation due to electrostatic charges or agglomeration due to clusters strongly bonded. One would anticipate that electrostatic flocculation would have been largely eliminated during backwashing and conditioning. The extent of agglomeration in a resin will be indicated by the fraction retained on a U. S. No. 16 sieve during a subsequent size determination.

It has been observed that smaller-bead resins are generally more uniform in shape than larger-bead resins. Shape irregularities are a factor leading to increased pressure drops because they impede classification of the resin bed; however, unless the resin is markedly non-uniform in shape, other considerations such as bead size and the form of the resin are usually more significant (1). Were two or more submitted lots found comparable in other characteristics, the lot observed to have the fewest shape irregularities would be selected for purchase.

To assist in continuously evaluating bead shape during a resin's service life, a shadow-printing technique is recommended. Not only the shapes but also the comparative sizes of several hundred beads can be recorded on one 8x10-inch shadow print. The technique is particularly useful as an indication of the extent of bead fragmentation occurring during cyclic expansions and contractions.

SIZE

Microscopic measurements. The most direct measure of size is obtained by measuring individual resin beads under a microscope at 50 - 100X. For irregularly shaped beads the microscopist's technique in selecting the axis of measurement is somewhat subjective; however, a resin with numerous odd-shaped beads would likely be rejected for purchase aside from size considerations.

As an example of data obtained by microscopic sizing, data in Table 1 were obtained with a sample of Amberlite IRC-50.

Table 1. --Microscopic Measurements of Amberlite IRC-50

Size, mm.	Number	Size, mm.	Number
.75	1	.51	4
.69	1	.50	12
.67	1	.49	4
.66	6	.48	2
.64	2	.47	5
.62	5	.46	4
.61	1	.45	1
.60	2	.44	3
.59	5	.43	2
.58	6	.42	4
.56	5	.41	2
.55	4	.39	5
.54	2	.35	2
.53	3	.31	1
.52	3	.30	1
		.26	1

From the above data the mean bead size was calculated to be .517 mm.

While measuring to .01 mm. is recommended, the data can be rearranged into intervals of .05 mm., as in Table 2, to simplify calculations without a significant loss in accuracy.

Table 2. --Condensed Version of Table 1

Size, mm.	Number	Size, mm.	Number
.705-.755	1	.455-.505	27
.655-.705	8	.405-.455	12
.605-.655	8	.355-.405	5
.555-.605	18	.305-.355	3
.505-.555	16	.255-.305	2

Using the mean of each interval as the size of its beads, a mean bead size of .517 mm. is again obtained.

In size measurements on resins, data are usually summarized in terms of effective size and uniformity coefficient; i. e., the 90 percent cumulative size in millimeters and the ratio of the 40 percent cumulative size to the 90 percent cumulative size, respectively. For normal distribution, the mean bead size, standard deviation, effective size, and uniformity coefficient are related as follows:

$$E.S. = \bar{x} - 1.28s$$

$$U.C. = \frac{\bar{x} + 0.25s}{\bar{x} - 1.28s}$$

$$= 1 + \frac{1.53s}{\bar{x} - 1.28s}$$

$$= 1 + \frac{1.53s}{E.S.}$$

where:

E. S. is the effective size;
$\bar{x}$ is the mean bead size;
s is the standard deviation;
U. C. is the uniformity coefficient.

Inspection of the data in Table 2 indicates the effective size is approximately .40 mm. The question is, how accurate are these quantities when they are calculated from measurements of 100 beads?

The mean size of the 100 beads was .517 mm. From experience it is known that size measurements of resin beads have a normal distribution. Assuming that the microscopist has sampled randomly, the standard deviation of this distribution is .094 mm. The standard deviation of the distribution of mean bead sizes of this resin, when each mean is obtained from 100 measurements, can be estimated as .094 mm. / $\sqrt{100}$, or .0094 mm. The 95 percent confidence interval of the mean bead size of the entire sample or lot of resin is then .517 mm. ± (1.96) (.0094 mm.), or .499 mm. to .535 mm.

Using this mean bead size interval, the 95 percent confidence interval of the effective size can be calculated to be .38 mm. to .42 mm. Similarly, the 95 percent confidence interval of the uniformity coefficient is calculated to be 1.35 to 1.38.

As indicated in Table 3, one does not appreciably decrease the 95 percent confidence intervals of the effective size and the uniformity coefficient by measuring more than 100 beads unless the standard deviation decreases upon further counting.

Table 3. --95% Confidence Intervals of Mean Bead Size and Effective Size

n	s(mm.)	u(mm.)	Effective Size (mm.)
100	.15	$\bar{x} \pm .030$	$\bar{x}$ - .22 to $\bar{x}$ - .28
	.10	.020	- .14 - .18
	.05	.010	- .07 - .09
500	.15	$\bar{x} \pm .013$	$\bar{x}$ - .23 to $\bar{x}$ - .26
	.10	.009	- .15 - .17
	.05	.004	- .08 - .09

where:
n is the number of measurements;
s is the standard deviation of n measurements;
u is the mean bead size of the entire sample or lot;
$\bar{x}$ is the mean bead size of n measurements.

The resin used in this example is specified by the manufacturer as having an effective size of .33 mm. to .50 mm. From measurements of 100 beads to .01 mm., it was ascertained that the effective size is within specifications. Concurrently, the microscopist was able to make qualitative observations of bead shapes. The data in Tables 1 and 2 is not presented as typical of IRC-50; the resin purchaser may require a resin with an effective size nearer .50 mm.

Wet sieving. Size measurements of resins are most commonly made with 8-inch-

diameter sieves. This enables the analyst to use greater quantities of resin in a size determination and places less emphasis on technique than do microscopic measurements. Usually recommended are U. S. Standard Sieves No. 16, 20, 30, 40, 50, and occasionally 60 or 70. The sieving process in a manual procedure consists in placing about 150 ml. of resin on the No. 16 sieve, moving the sieve up and down in a pan of water for a specified time or number of immersions so as to pass sub-size beads through the sieve, and rinsing the effluent resin onto the next sieve in the series. The resin retained on each sieve is transferred to graduated cylinders of suitable size and measured volumetrically. The last sieve in the series should be of such size as to collect any resin passing through the No. 50 sieve.

Cumulative totals for each sieve may be plotted on probability paper, either logarithmic or arithmetic. Since the range of size data for resin samples is often over only one decade, the latter paper is usually sufficient. One must sometimes approximate the data by a straight line in the fine range or even over the entire range. This approximation is necessary if coarse and/or fine beads have been removed either during manufacture or during subsequent conditioning or use of the resin, making the distribution no longer normal.

The effective size of the resin is the ordinate value of the line intersection at the 90 percent cumulative size. The uniformity coefficient is the ratio of the 40 percent ordinate value to the effective size.

Analyst time required for wet sieving can be reduced considerably by using a mechanical shaker for the initial separation. Experience with a "Pulverit 3" (Geoscience Instruments Corp.) indicates that operating conditions can be determined which give results comparable to those obtained by an entirely manual procedure. The "Pulverit 3" accomodates up to six sieves and can be set at varying amplitudes of electromagnetic vibrations, arbitrarily designated from one to ten. Wet sieving is accomplished through use of a spray nozzle inserted through the cover above the topmost sieve. Operation of the instrument at an amplitude of one for thirty minutes will separate a sample of about 75 ml. The transfer and measuring operations must still be done manually; however, these operations consume less time than does the separation.

The resin sample must be initially spread over as large an area as possible in order to minimize clumping. High and even moderate amplitudes lead to vibration patterns which impede separation. Separation is less precise than that obtained through an entirely manual procedure; however, the gain in analyst time is twofold. If the laboratory has two sets of sieves, the second sample can be separated while the first is being transferred and measured. The data in Table 4 is representative:

Table 4. --Manual Procedure vs. Geoscience "Pulverit 3" Sample: Amberlite IRC-50

U. S. Sieve	Nominal Size, mm.	Manual	PULVERIT 10-min.	PULVERIT 20-min.	PULVERIT 30-min.
16	1.19	0.8	0.3	0.4	0.4
20	0.84	5.4	13.3	9.1	5.4
30	0.59	50.0	50.0	43.5	40.4
40	0.42	92.4	90.1	90.4	89.4
50	0.30	99.2	97.6	99.0	99.3
E. S. *		0.44	0.41	0.43	0.43
U. C. *		1.45	1.63	1.51	1.44

*From plot on arithmetic-probability paper

CYCLICAL EXPANSIONS AND CONTRACTIONS

Evaluation of a resin should include measurements of expansions and contractions which occur during conditioning or regeneration. For example, Amberlite IRC-50 expands when converted from the hydrogen form to the sodium form and contracts when cycled back to the hydrogen form. The data, ex-

pressed in terms of net expansions and percentages of fines formed during cycling, is an indication of the strength of the resin beads. Cyclical expansion characteristics must be known in order to determine both the volume of resin that a bed can accommodate and the theoretical total ion exchange capacity of a resin bed. These characteristics must also be known in order to predict the expansion which will occur during separation of two resins in a mixed-bed system, as well as the degree and ease of separation. Expansions near or above the manufacturer's stated maximum indicate potential problems during backwashing and regeneration in operational systems.

Volume changes are temperature- and pH-sensitive and may vary from cycle to cycle; therefore, the laboratory test must be standardized. A typical test consists of measuring the volume of a resin bed after treatment with five-bed volumes of 1N NaOH and 1N HCl. The initial volume measurement must be made after the sample has come to a full swell in water and has been backwashed to remove fines. Measurements to 10 ml. can conveniently be made if the test is conducted in a 1000-ml. dispensing buret; prior to each measurement, the excessive acid or alkali is rinsed out and the resin is backwashed, allowed to settle, and drained of water above the top of the bed. The temperature at which the test is conducted should be the temperature at which the resin is regenerated in the operational system.

During this test an estimate of the percentage of fines formed during each cycle can be made concurrently. Table 5 contains illustrative data.

DECOLORIZATION

Decolorization with resins generally occurs either in a mixed bed system as an adjunct of deionization at temperatures less than 120° F. or in a system designed primarily for decolorization at 160°-170° F. In the decolorization system, a lesser amount of a strong cationic resin in the sodium form might also be employed to soften liquors by exchanging sodium for calcium and magnesium. This use of resins, to decolorize sugar liquors, has been described as an example of van der Waals adsorption rather than of ion exchange (2). A highly porous, strongly basic anion exchange resin in the chloride form removes from solution color bodies of high molecular weight. Anion exchange resins with less porosity have a lower color removal efficiency. The anionic resin in the chloride form will also exchange chlorides for sulfates, phosphates, and other anions.

Unlike measurements of ion exchange capacity, in which standard reagents are employed, laboratory measurements of color removal efficiency are significant only when made on process liquors of interest. The variability of color bodies in process liquors indicates that resins should be tested with liquors of diverse origins. One way of doing this is to take the influent liquor daily from process streams over an extended period of time. Further, a decrease in color removal efficiency may be sudden rather than gradual; therefore, an acceptable resin should be tested simultaneously, so as better to evaluate variations in influent liquors.

It is suggested that laboratory testing of a resin unfamiliar to the processor encompass a minimum of 40 cycles before the resin is accepted for purchase. This large number of test cycles is necessary because several cycles may be completed before certain objectionable side effects, such as sucrose inversion or increased color throw, become apparent.

A typical decolorization cycle consists of sweetening on, displacement of 60 bed volumes, sweetening off, regenerating with sodium chloride, and rinsing with water. During these laboratory operations, all linear velocities should approximate process linear velocities.

While a pilot plant operation might util-

Table 5. --Expansion (and Contraction) of IRC-50
During Cycling at 80° F.

	Volume (ml.)	Net Expansion %	Fines Formed %
1. Sample before backwash	630	--	--
2. Sample after backwash	620	--	1.6
3. Volume taken for test	380	--	--
4. After 2000 ml. 1N NaOH	680	79	--
5. After 2000 ml. 1N HCl	500	32	--
6. After 2000 ml. 1N NaOH	700	84	< 1.0
7. After 2000 ml. 1N HCl	560	47	--
8. After 2000 ml. 1N NaOH	770	103	< 1.0

ize 400-500 ml. of resin and 7.5 gallons of liquor throughput per cycle, a typical laboratory cycle consists of flowing 3000 ml. of liquor through 50 ml. of resin. It is preferable to collect the effluent liquor in three 1000 ml. fractions and to determine the color removal efficiency for each fraction within the cycle. The influent liquor and the three effluent fractions are also analyzed for solids content and pH. Regeneration with sodium chloride and subsequent rinsing should follow collection of the effluent as soon as possible in order to minimize microbiological activity.

During regeneration a certain amount of adsorbed color bodies may not be removed by sodium chloride. The processor may consider it necessary occasionally to supplement regeneration with a dilute solution of an oxidizing agent such as sodium hypochlorite. Such an oxidizing agent will degrade the structure of the resin bead, increase bead porosity, and make subsequent regeneration with sodium chloride more effective. If an oxidizing agent is periodically used in processing, it is certainly advisable, when testing an unfamiliar resin, to complete a sufficient number of laboratory cycles to make its use necessary.

When an oxidizing agent is used as a supplementary regenerant, a balance must be achieved between effective regeneration and minimum impairment of the integrity of the resin beads. The former is measured by the color of the effluent in subsequent cycles; the laboratory should continuously evaluate the latter, either microscopically or by determining if the moisture content of the resin beads has increased significantly.

During decolorization a decrease in effluent pH may indicate degradation of the functional sites of a quaternary ammonium resin to tertiary amine groups.

The following outlines a procedure for a laboratory decolorization cycle:

1. Place 50 ml. of a conditioned resin in a column with suitable provision for maintaining resin temperature at 160°-170° F. Resin height should approximate 15-20 cm. Drain water to top of resin.

2. Sweeten on with the process liquor of interest (57-60 Brix, 160°-170° F) and adjust flow rate to 18-20 ml./min. After the effluent density reaches 50 Brix, collect three 1000-ml. fractions.

3. Drain excess liquor to top of resin.

Sweeten off with hot water (160° - 170° F) until effluent is sugar-free. Drain water to top of resin.

4. Regenerate with 100 ml. of 10% sodium chloride (160° - 170° F) at 6-7 ml./min.

5. Rinse with hot water (160° - 170° F) until effluent is negligible in chloride content. (Rinse requirements vary with resin and cycle.) Drain water to top of resin.

6. Regeneration with sodium hypochlorite supplements regeneration with sodium chloride at the completion of every tenth cycle as follows:

   a. Regenerate and rinse as in 4 and 5 (above).
   b. Rinse with 100 ml. of cold water at 6-7 ml./min.
   c. Regenerate with 150 ml. of 0.5% sodium hypochlorite (less than 90° F) at 10 ml./min.
   d. Rinse with 100 ml. of cold water at 6-7 ml./min.
   e. Regenerate and rinse as in 4 and 5 (above).

Concerning measurements of color, the individual laboratory may decide upon a relatively rigorous method, e.g., one of the spectrophotometric methods outlined in ICUMSA (1958) (3), or a visual method, such as the liquid color standards used by SuCrest Corporation in process control (4). The latter are solutions of mineral salts in dilute hydrochloric acid arbitrarily designated from zero to thirty. Each color standard has been correlated as equivalent to so many color units, a color unit being defined as the absorption index, at 500 nm. in a 1-cm. cell, multiplied by 1000. For example, a standard of 14 corresponds to 22 color units, while a standard of 3-4 (or 3+) corresponds to 3.6 color units. If these are the colors of influent and effluent liquors, respectively, the percentage of color removed is 84. If resin volumes, column diameters, temperatures, and flow rates have been equalized for a standard resin and for the resins being tested, the color removal efficiencies of the resins are proportional to the percentages of color removed by the resin.

The data in Tables 6 and 7 were obtained using both "Tentative Solution Color Method 1-A," ICUMSA (1958) and the aforementioned visual color standards. Each of three resins was subjected to 20 laboratory cycles with influent liquors taken daily from process streams. The three resins had approximately equal color removal efficiencies through the tenth cycle; consequently, data is detailed only for Cycles 11 through 20. It is noted that at the end of 20 cycles, Resin A appears to be a less efficient decolorizer than either Resin B or Resin C, particularly after Cycle 14. Further testing will be required to distinguish between Resin B and Resin C, although the latter was comparatively less efficient on Cycle 20.

Table 7 shows that the color removal percentages calculated from the particular visual standards used are consistently 3-5% higher than values obtained by Method 1-A; however, the relative rankings of the three resins by either method are equivalent. While visual standards have obvious deficiencies, their use in this particular application does provide information sufficiently accurate for simultaneous evaluation of several resins. It is also true that influent color values obtained by Method 1-A are likely less reliable than are effluent color values, since the method is stated to be "for White Sugar and Sucrose-Type Liquid Sugars."

Whether an instrumental or a visual procedure is used, adjustment to 7.0 ± 0.2 pH is necessary prior to color measurement.

Occasionally, some of the color bodies adsorbed by the resin may not be removed during regeneration and subsequent rinsing but may be leached out during sweetening on. Such color throws may be caused by density and viscosity gradients occurring during sweetening on. While these color throws are infrequent, it is advisable to test an unfamiliar resin for this eventuality. This may be

Table 6. --Decolorization with Resins A, B, and C

COLOR OF ON LIQUOR			COLOR OF OFF LIQUORS					
			Resin A		Resin B		Resin C	
Cycle	1-A*	Visual**	1-A	Visual	1-A	Visual	1-A	Visual
1	226	16+	27	2+	23	1+	19	1+

5	199	16+	21	1+	26	2+	21	2

11	165	14+	26	2+	14	0+	20	0+
12	155	14+	27	2+	23	1+	21	0+
13	119	13+	27	3	22	1+	19	1+
14	136	14	43	5+	19	1+	26	2+
15	142	14	31	5	27	2+	18	1+
16	145	14+	53	8+	20	1+	37	4+
17	147	14+	40	4+	34	4+	26	2+
18	212	15+	39	4+	24	2+	22	1+
19	142	14+	26	3	23	2	18	1+
20	200	16	67	10	16	1+	54	8+

*Tentative Solution Color Method 1-A, ICUMSA (1958). Values are expressed in color units.
**Liquid color standards used by SuCrest Corporation.

Table 7. --Percentage of Color Removed by Resins A, B, and C

	Resin A		Resin B		Resin C	
Cycle	1-A	Visual	1-A	Visual	1-A	Visual
1	88	91	90	94	92	94

5	89	94	87	91	89	93

11	84	88	92	95	88	95
12	83	88	85	92	86	95
13	77	82	82	89	84	89
14	68	75	86	91	81	87
15	78	76	81	87	87	91
16	63	68	86	92	74	81
17	73	81	77	81	82	88
18	82	84	89	90	90	93
19	82	86	84	90	87	92
20	67	73	92	95	73	75

done by sweetening on with a syrup of very low color and measuring the color of the first portion of the effluent.

DEIONIZATION

Ion exchange resins have maximum capacity values, expressed in terms of eitner the scientific weight capacity (meq. /gram of dry hydrogen or chloride form) or the technical volume capacity (e. g., eq. /liter of packed, fully water-swollen hydrogen or chloride form). These maximum values can be calculated for certain combinations of matrices and ionic groups (5). For example, a polystyrene resin with about 8 percent divinylbenzene, such as Amberlite IR-120 or Duolite C-20 would, when completely sulfonated, be composed of $C_8H_8O_3S$ units, which have a formula weight of 184. 2. The maximum capacity of such a resin, expressed in terms of scientific weight capacity, would be approximately 1 meq. /0. 1842 g., or 5. 4 meq. /g.

The manufacturer's specifications list capacities nearer 5. 0 meq. /g. for the aforementioned resins; however, the latter capacities are more properly designated as apparent (or effective) capacities and are dependent upon experimental conditions. Experimental conditions are particularly critical when one determines apparent capacities of weak cationic resins. For example, the capacity of Amberlite IRC-50 is about 10 meq. /g. (dry) in alkaline media, about 7. 8 meq. /g. in neutral solutions, and negligible at a pH of 3. 5.

Of more interest to the processor are breakthrough capacities, which might be expressed in kilograins of $CaCO_3$ per cubic foot of resin (wet) or in pounds of "ash" removed per cubic foot of resin (wet). As a practical control, the processor monitors the conductance of the effluent liquor and ends the cycle when the conductance reaches a predetermined value, e. g., 7 micromhos. The breakthrough capacity, calculated from throughput and influent and effluent ashes, may be only a fraction of the apparent capacity determined by standard methods. If the apparent capacity greatly exceeds the breakthrough capacity, there is less significance attached to measurements of apparent capacities and more to analyses of effluent liquors. Consequently, one often determines apparent capacities of replacement resins more to verify specification data rather than to predict the performance of the resin in an operational system.

Methods for determining ion exchange capacity are detailed in several well-known sources (6, 7, 8). Measurement of the deionizing ability of a resin in the sugar industry is not only a matter of determining the apparent capacity but is also dependent upon bead size, shape, strength, and miscellaneous process variables. It is better evaluated by frequently obtaining information concerning throughput and ash content of the influent and effluent liquors. As with measurements of color removal efficiency, it is desirable to compare one resin with another whenever possible.

The following data summarize early plant performance of two strong anion resins from different manufacturers. Each resin, in the hydroxide form, was used in a mixed-bed system in conjunction with a weak cation resin in the hydrogen form. The total volume of resin in each bed was 170 cubic feet.

From the data in Table 8, Resin A appears to be a significantly better deionizer than Resin B; however, the relative costs of the two resins must be taken into account. In this particular example, Resin A cost about 25% more than Resin B; the cost increase paralleled the increase in throughput. Comparative testing of these two resins is, of course, continuing.

During the service life of a resin, breakthrough capacity may decrease either because of a loss of functional sites or because of a loss of resin during backwashing and regeneration. Thus a premium is placed upon bead strength, the ability of a resin to withstand stresses applied during expansions and contractions. An indication of bead strength

Table 8. --Mixed-Bed Performance of Resin A and Resin B

	Resin A	Resin B
Number of Cycles	17	17
Average Influent Brix	58.0	57.9
Average Influent Ash %	0.122	0.124
Average Lbs. Solids Throughput	102,009	83,164
Average Lbs. Ash Removed per Cycle	124.5	103.1
Average Lbs. Ash Removed per ft^3 resin	0.72	0.58
Breakthrough Capacity Meq./ml.	0.20	0.16

can be obtained by periodically determining the moisture content of the resin during its service life. Increases in moisture content indicate degradation of the bead structure, particularly through loss of cross-linked divinylbenzene.

SUMMARY

Evaluation of a resin initially consists of measurement of physical factors such as shape, size, and strength, the latter determined from cyclical expansion data. In evaluating the ability of a resin to deionize or decolorize, it is necessary to work with actual process liquors. The fact that process liquors have wide variance makes extensive testing necessary. A laboratory testing program can be at least an adjunct of previous pilot plant studies, at most a starting point for new pilot plant studies leading to process improvements.

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DISCUSSION

H. M. Wallenstein (Refined Syrups): Which single one of these properties is most in need of improvement?

R. D. Moroz (SuCrest): The property that we would like to see improved most at SuCrest would be the relationship between bead size and few shape irregularities. We would like to see very large bead size in our beds. However, when the manufacturer tries to make a very large bead size, he ends up with very many irregular shapes. This is just as bad as working with small bead size. I would say from my experience that bead size is very important.

S. Stachenko (C&D): You have indicated a lab technique for evaluating color removal. Did you find the technique to correlate well with your plant practice?

R. D. Moroz: Yes, we have. Of course, we had to make modifications in the laboratory over the years. I think that this procedure was developed about 18 years ago, and I think that it has been in its final form for 8 years or so now, and it agrees quite well with our plant performance. I might add, though, that other refineries might work somewhat differently. The procedure that we outline here, of course, works fine for us. I am not saying that this will work all the time for everybody.

K. J. Parker (Tate & Lyle): I would like to be permitted to make a point in this connection.

In evaluating resins for decolorization, particularly where one is comparing two resins which may be rather different, the results you get might well depend on the method of color measurement you employ. I can quote, from our own experience, a particular example of this. If 3 standard methods for measuring the color of the effluent were used, they lead to three possible conclusions: that there is no difference between the resins; that one is twice as effective as the other, and vice versa. This really raises a very profound question of what do you mean by the efficacy of the particular resin. This is best illustrated in Figure 1, where the situation is exaggerated a little just for purposes of illustration. This can actually happen. If one considers the visible light absorption spectra of color, in the range of about 400 to 600 nanometers, and in the form of a smooth Curve I as shown in Figure 1, another effluent from an ion exchange column could differ by having the shape of absorption curve shown by curve II in Figure 1.

The question of which has the higher color depends upon the wave length of measurement. In Figure 1, the two solutions have the same color at wave length A, while at the higher wavelength, C, No. I is more colored and at the shorter wavelength, B, No. II is more colored.

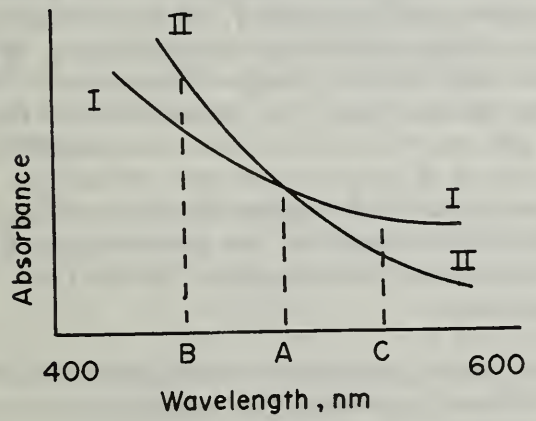

Figure 1. Absorption Curves of Two Effluents.

The question is, which is the higher color? Well it all depends upon what you mean by color. One can actually get this result if you were to compare for example, Amberlite XE 258 with Amberlite IRA 401. This raises a doubt, when one is considering the validity of comparisons of two very dissimilar resins with a liquor of unknown color constitution.

R. D. Moroz: I am in agreement with Dr. Parker, and I would like to bring out another point. We are using visual color methods for this specific reason. We sell to a customer who doesn't give a darn what the value is according to a machine. He says that if this color is dark to me, it is dark, or this color has brown tones or yellow tones. This is a selling point, so we try to stay with this visual method, which was developed, by the way, back in 1925 in Berlin. Now there is another type of color here, which we have not discussed, and that is color precursors, which are not colored to the eye, but from which a very dark color will form later, upon evaporation. We have tried to devise methods where we could predict the formation of color precursors.

K. J. Parker: I am very interested to know that you do recognize these color precursors; they are very important and I shall, tomorrow, have the honor of speaking to you, and this is one of the points that I shall be talking about.

THE REFINING OF CANE SUGAR BY ION EXCHANGE

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INTRODUCTION

The continued or prolonged application of a particular technique or technology to an industrial operation occasionally runs the risk that it is applied routinely by many without full realization of its basic function, thereby hindering the progress of new developments. The sugar industry, among others, finds itself within this situation, at times, with respect to the use of adsorbents and ion exchangers. It is therefore of some importance that we focus attention, in this respect, on some basic principles involved in the use of such sugar refining aids.

The use of adsorbents and ion exchange materials was pioneered by the sugar refining industry before any other industry. In fact, much of the early research on adsorption and ion exchange was conducted with the ultimate purpose of employing these techniques in sugar refining. In applying these techniques, various adsorbents were explored, at first, for their ability to remove impurities from sugar syrups in order to obtain a purer sugar and later to obtain greater yields of pure sugar. Attention was focused on the removal of colored impurities and the various carbonaceous adsorbents, particularly bone char, became the major refining aid in the cane sugar refining industry.

In more recent years, the true value and function of bone char has become more apparent. Not only does the bone char remove color from the cane sugar syrups but it may also remove a portion of the ash impurities. The technology surrounding the use of bone char has been developed to the point where it can be applied routinely and effectively without destroying any of the sucrose values through inversion. The structure of bone char is such that it also is effective in removing haze and some invert sugar that is present in the cane sugar syrup that is to be refined. These functions of bone char are not surprising in view of the physical and chemical structure of bone char; however, the de-ashing function of the bone char, although of low capacity, is not generally realized under all conditions. In fact, the de-ashing capacity of the char is often exceeded yielding effluents from which no ash has been removed.

At a previous meeting (Montreal, 1959) of the Bone Char Research Project, one of the authors (Kunin) speculated as to the function of bone char attributing the decolorization and ash removing properties to its hydroxyapatite chemical structure and its porous physical structure. The role of hydroxyapatite as an ion exchanger and an adsorbent is well-known. It is of interest to note that hydroxyapatite is, in reality, employed three times in the processing of cane sugar. During the liming of raw cane juice and during the defecation of the affination syrup, hydroxyapatite is formed and functions, to some extent, as it does when employed as bone char. Although many agree with this theory, others attribute the function of bone char to its carbon matrix. It is obvious that neither group of theorists on the function of bone char can be entirely correct, since one might conclude from the negative conclusions of both groups that neither the carbon nor the hydroxyapatite are essential, and that the remainder, the pore structure, as facetious as it may appear, is the important factor.

Of course, the above remarkable functions of bone char in sugar refining are not achieved without some payment. The capacity of the bone char to perform these functions is not very high, and considerable investment in equipment is required for the furnace or kiln operation that is required for the regeneration or rejuvenation of the

char. Large furnaces, extremely low flow rates, and large bone char units are required to realize the full capacity of the chars. In many respects, some of the same problems are encountered with granular carbons. These are serious limitations and have become more serious in recent years as expansions of plant facilities are considered.

If one examines the bone char operation, an obvious question to ponder concerns itself with the possibility of devising other adsorbent systems that will perform the functions of bone char but will not require the furnaces or "retorts" for regeneration,and perhaps will perform these functions more effectively with respect to capacity and degree of purification. One need not recall for the sugar industry the potential of ion exchange for refining sugar. Ion exchange was actually studied by the sugar industry before it was employed for water treatment. Ion exchange resins are now employed successfully on a modest scale throughout the sugar industries of the world for the refining of beet, corn, and cane sugar. Ion exchange resins are employed for both the decolorization and deionization or de-ashing of cane sugar syrups. In most instances, however, ion exchange resins, when used on cane sugar syrups, are employed primarily to supplement the functions of bone char. On some occasions, ion exchange resins coupled with the use of granular or powdered carbons have been employed to replace the bone char operation.

The decolorization and deionization properties of various ion exchange resins for producing the pure liquid syrups from cane syrups have been well described in the literature and need not be reviewed here. It is quite obvious from the wealth of available information that ion exchange materials may be employed to remove practically all the impurities present in cane juices and syrups. If there is any outstanding singular feature of ion exchange resin technology as applied to sugar refining, it is the basic ability of ion exchange resins to effectively decolorize and deionize syrups and juices at higher flow rates.

In view of the wide experience that has been accumulated with ion exchange resins in the sugar industry, one might ask why ion exchange has not progressed more in the refining of cane sugar. It does not take much thought before one will conclude that, to progress further in the area of cane sugar refining, ion exchange will have to perform more effectively and economically than other adsorbents, bone char in particular. If such an ion exchange system can be devised, it must pass several requirements:

1. The system should decolorize and de-ash the cane sugar syrup following the defecation and clarification stage.
2. The ion exchange system should accomplish these functions at elevated temperatures without significantly increasing the invert sugar.
3. Regeneration of the ion exchange system should be relatively simple and economical.
4. The ion exchange resins should be quite stable and resistant to fouling.

In view of the considerable experience accumulated to date with cation exchange resins on the inversion of sugar and the stability and fouling of anion exchange resins employed in the deionization and decolorization of sugar liquors, the above requirements lead one to the following conclusions concerning the possible choice of an ion exchange resin system:

1. Sulfonic acid cation exchange resins cannot be used because of their high catalytic activity for inverting sucrose.
2. The cation exchange resin will have to be a weak acid cation exchanger such as a carboxylic acid cation exchange resin.
3. The carboxylic acid cation exchange resin will have to be used in a mixed-bed or Monobed system since this ion exchange resin is still capable of inverting sucrose when used by itself,due to the generation of ion exchanged acidity.
4. The anion exchange resin will probably have to be a porous, weak base anion exchange resin, preferably posessing a tertiary amine structure.

These conclusions are based upon the fact

that all cation exchangers in the hydrogen form (this is the form required for de-ashing) will invert sucrose at rates in excess of desirable limits if employed at the elevated temperatures being considered. The only hope of employing a cation exchange resin would be to employ the carboxylic acid type in a Monobed. The high temperature and regeneration requirements lead one to select the tertiary amine weak base anion exchange resin. The primary and secondary amine structures are unstable in the presence of invert sugar. Finally, since both ion exchangers are weak electrolytes, equilibrium considerations dictate the use of a Monobed or mixed-bed. These restrictions are, in fact, so severe that one might conclude that the use of ion exchange resins under such conditions might be impractical. This reasoning leaves one with very few degrees of freedom or choice. If one also considers the fact that the basic strength of weak base anion exchange resins decrease with increasing temperature, equilibrium considerations might discourage one from this basic approach. Recent developments, however, in ion exchange resin technology, have given some encouragement to the possible effectiveness of this proposed system.

With this background, an exploratory laboratory study was conducted for the purpose of determining the optimum conditions for operating the Monobed of the weak electrolyte ion exchange resin system for the purpose of decolorizing and de-ashing of the cane sugar syrups, and for the purpose of comparing its performance with bone char.

EXPERIMENTAL STUDY

Ion Exchange Resins - Previous experience led to the selection of Amberlite IRC-84 and Amberlite IRC-50 as the carboxylic acid cation exchange resins and Amberlite IRA-93 as the weak base anion exchange resin. These products have been widely employed for years in water treatment. Amberlite IRC-50 and Amberlite IRA-93 are macroreticular ion exchange resins. Amberlite IRC-50 has been used widely in the pharmaceutical industry while Amberlite IRA-93 has been used extensively in the deionization and decolorization of beet and cane juices and syrups. The characteristics of these ion exchange resins are described in Table 1.

Bone Char Samples - Samples of virgin and revivified Synthad and revivified bone char were kindly supplied by Refined Syrups (Yonkers, New York).

Several other macroreticular anion exchange resins were studied and their pore structures are described and compared with bone char in Table 2.

Sugar Liquors - For this laboratory study, the cane sugar syrups were supplied through the courtesy of Refined Syrups (Yonkers, New York) and the feed to the bone char unit was selected for study. Some experimentation was performed on samples of the effluent of the bone char units. The characteristics of the liquors are described in Table 3.

Analytical Methods - Color measurements were made visually using standards. The conductivity and pH methods were those normally employed by the sugar industry. Metal analyses were performed by means of atomic absorption. Invert sugar analysis was conducted by the method described by the National Bureau of Standards.

Experimental Details - The decolorization and deionization experiments were conducted in jacketed columns, 1/2" inside diameter. The bed depths were approximately 2 feet. The flow rates were approximately 0.1 gal./cu. ft./min. for the bone char runs and 0.25 gal./cu. ft./min. for the ion exchange resin runs. These correspond closely to the rates normally used with these ion exchange materials in the cane sugar industry. It was fully realized that such conditions were not favorable to the use of bone char in that normally much deeper beds and lower flow rates are employed; however, the conditions normally employed would have been impractical for a laboratory study.

A survey of the various papers in the Proceedings of the Project over the past decade reveals the use of variable flow rates ranging from

Table 1. --Properties of Amberlite Weak Electrolyte Ion Exchange Resins

Characteristics	Amberlite IRC-84	Amberlite IRC-50	Amberlite IRA-93
Exchange capacity,			
meq./g.	11	10	4.8
meq./ml.	3.5	3.5	1.4
Particle size, mm.	0.38-0.46	0.33-0.50	0.4-0.5
pK_a (acidity)	5.3	5.9	-
pK_b (basicity)	-	-	5.3

Table 2. --Pore Structure Data

Characteristics	Bone Char	Amberlite IRC-50	Amberlite IRA-93	Amberlite XE-238	Amberlite IRA-900	Amberlite IRA-904
Skeletal density, s, g./cc.	2.76	1.34	1.10	1.15	1.14	1.11
Apparent density, a, g./cc.	1.51	1.13	0.58	0.58	0.89	0.56
Porosity						
cc./cc.	0.45	0.16	0.48	0.60	0.22	0.50
cc./g.	0.30	0.14	0.83	1.04	0.24	0.91
Surface area $m^2/g.$	69	1-2	21	7	16	42

Table 3. --Composition of Liquors

	Clarified Cane Sugar Liquor (Feed to Bone Char Units)		Bone Char Liquor (Bone Char Effluent)
	A	B	
Brix	60	60	60
pH	7.15	6.55	6.25
Specific Resistance,(1) ohm-cm.	8400	3200	8500
Na, (as $CaCO_3$)	15	24	22
K, (as $CaCO_3$)	90	416	96
Ca, (as $CaCO_3$)	180	305	90
Mg, (as $CaCO_3$)	56	56	129
Total	341	801	337

1. Specific resistance measured for 15 Brix solution after dilution of the 60 Brix liquors with D. I. water.

0.01 gal./cu. ft./min. to almost as high as that employed in this study. The optimum conditions selected for the operation of the Monobed are summarized in Table 4. From the information

Table 4. --Details for Operation of Amberlite IRA-93/Amberlite IRC-84 Monobed

1. Ratio $\frac{\text{Amberlite IRA-93}}{\text{Amberlite IRC-84}} = \frac{3}{1}$
2. Operational flow rate = 0.25 gal./cu. ft./hr.
3. Sequence of Monobed operation conducted at 60° C.
   a. Sweetening-On
   b. Exhaustion
   c. Sweetening-Off
   d. Backwash to separate Monobed Components
4. Sequence of regeneration operation conducted at 50° C.
   a. Regeneration of Amberlite IRC-84 with H_2SO_4 at 110% theory
   b. Rinse
   c. Partial exhaustion of Amberlite IRC-84 with NH_3 or NaOH at 10% theory
   d. Rinse of Amberlite IRA-93 with acidic-salt regeneration effluent from Amberlite IRC-84
   e. Rinse with 2 to 3 BV of H_2O
   f. Regeneration of Amberlite IRA-93 with NH_3 or NaOH at 110% theory
   g. Rinse
   h. Remix of Monobed components

in Table 4, it is obvious that the capacity of the anion exchange resin is the limiting component of the Monobed. The Monobed was operated through 12 cycles in the manner described in the literature for most Monobed ion exchange resin systems. In order to maintain the pH of the sugar syrup within the range pH 7-8 and in order to minimize inversion, the cation exchange resin, Amberlite IRC-84, was partially neutralized, following regeneration with H_2SO_4, to about 10-15% of its theoretical ion exchange capacity using NaOH or NH_4OH.

A few runs were made in which the effluent of the Monobed was further decolorized using quaternary ammonium anion exchange resins in the chloride form.

DISCUSSION OF RESULTS

The results of this investigation are summarized in Table 5 and Figures 1 through 10. The summarized results include data on pH, ash (conductivity), decolorization, and individual data on Na, K, Ca, and Mg. Sucrose inversion data are reported for the runs on the bone char and the Monobed at temperatures of 60, 70, and 80° C. The results are self-explanatory. They clearly indicate that the weak electrolyte Monobed satisfies the basic requirements set forth in the introduction. It is quite apparent that the Monobed has a greater capacity, at the flow rates studied, for treating more cane sugar syrups than bone char and yields a syrup of greater purity. The Monobed can fulfill this function with very little sucrose inversion. Further, the data indicate that both ion exchange resin components are stable under the conditions of operation. It is also quite obvious that the capacity of the Monobed is limited by the capacity of the weak base anion exchange resin. Analysis of the anion exchange resin effluent indicated that a capacity ranging from 0.14-0.24 eq. per liter was realized. This is only about 10-15% of the anion exchanger's theoretical capacity.

Although the capacity of the bone char runs (ca. 4 bed volumes) corresponds to a value as high as 25 lbs. char per 100 lbs. sugar, this value is higher than reported values of 5 lbs. char/100 lb. sugar obtained at the low flow rates. On the other hand, however, Project Proceedings over the years do report values as high as 25 lbs. even at low flow rates.

It would be beyond the scope of this preliminary study to make any conclusions as to the overall economic value of the weak electrolyte Monobed as a possible substitute for

Table 5. --Stability of Monobed Ion Exchange Resins

Characteristics	Amberlite IRC-84		Amberlite IRA-93		
	Before Cycling	After Cycling		Before Cycling	After Cycling
Moisture content, %	45.8	49.8		53.6	54.1
Ion exchange capacity, meq./g.	12.0	11.8	NH_3	4.32	4.29
			SO_4	0.33	0.20
			Total	4.65	4.49
Appearance					
physical	-	No change		-	No change
color	clear	Sl. discoloration		lt., opaque	lt., opaque

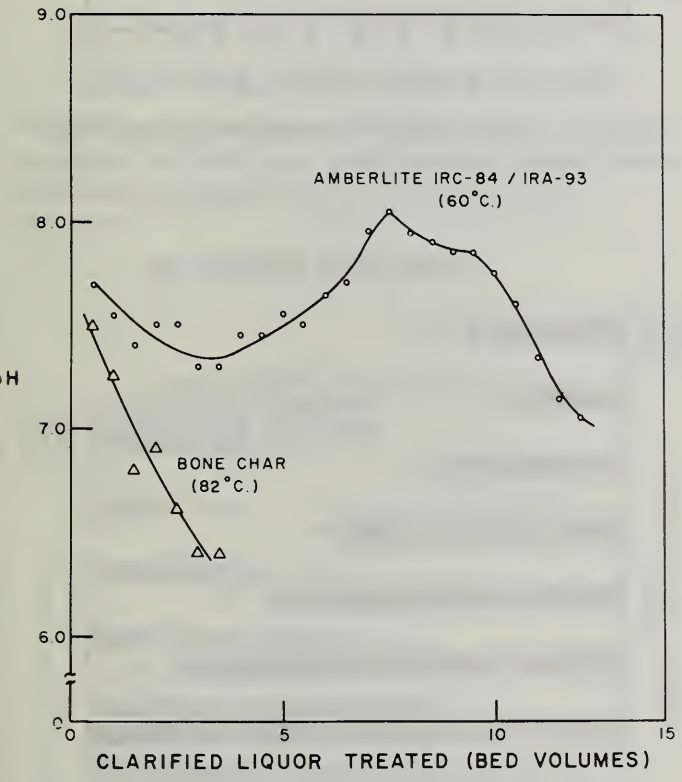

Figure 1. Comparison of pH of liquors off ion exchange and bone char

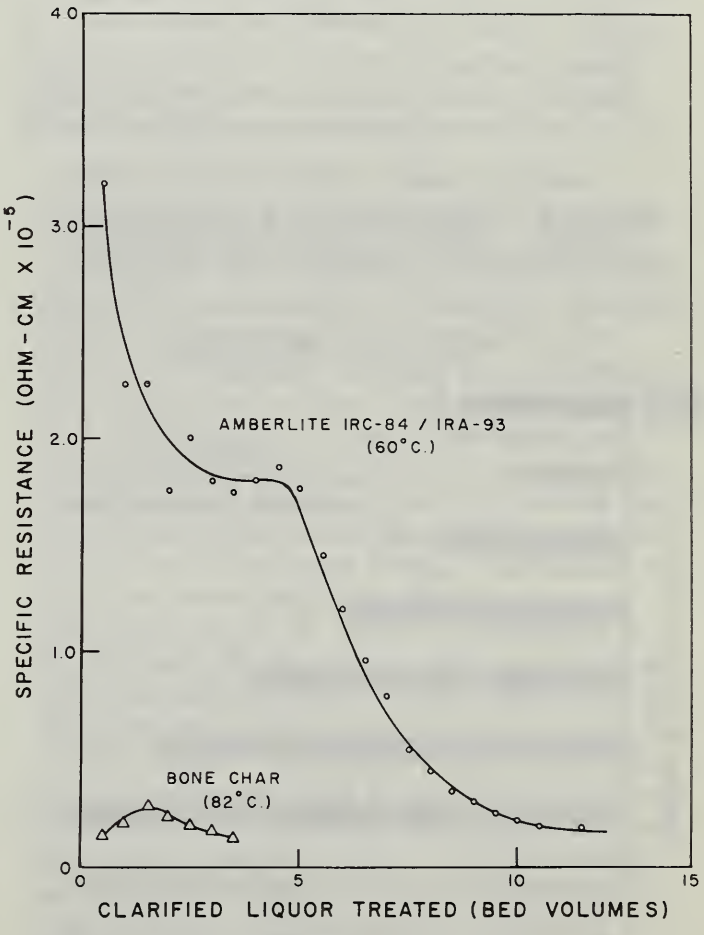

Figure 2. Comparison of Ash (Conductivity) of liquors off ion exchange and bone char

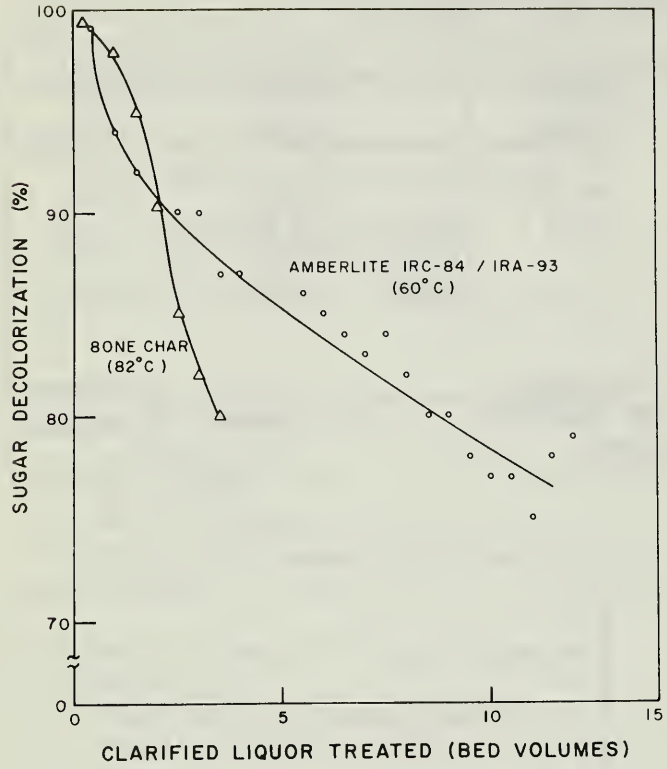

Figure 3. Comparison of decolorization of liquors off ion exchange and bone char

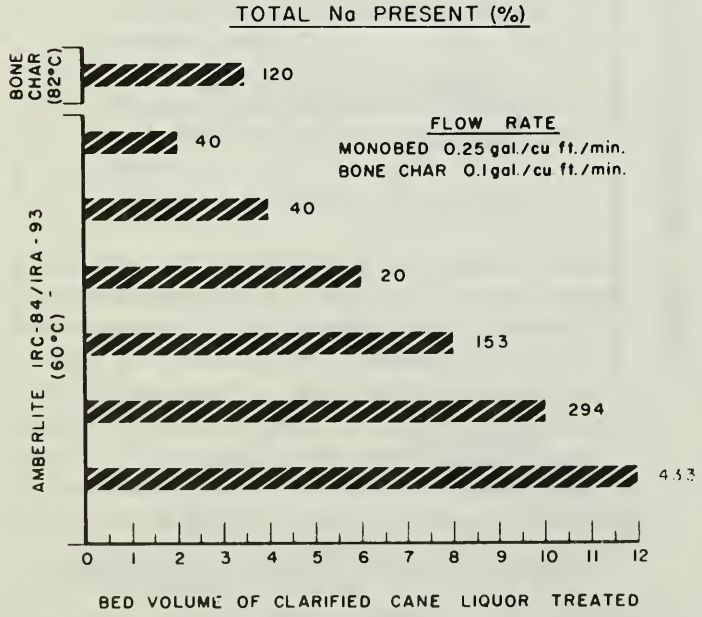

Figure 4. Comparison of sodium remaining in the liquor off ion exchange and bone char. Figures refer to amount present compared to on liquor at that amount of liquor treated.

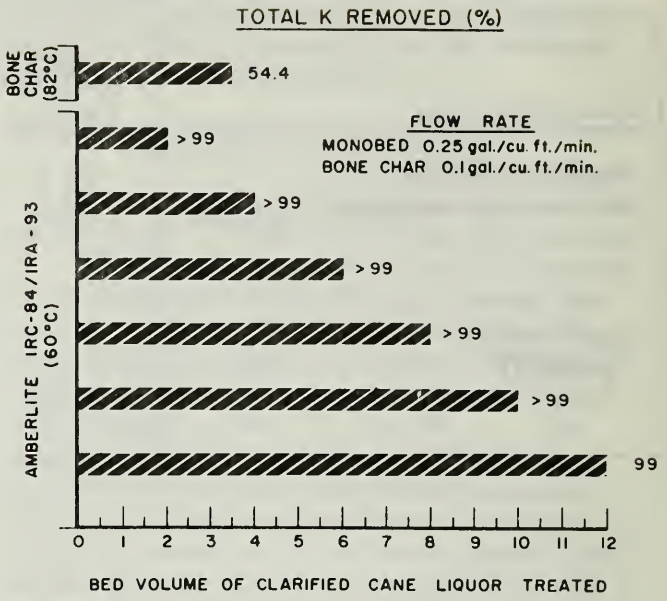

Figure 5. Comparison of potassium removed by ion exchange and bone char

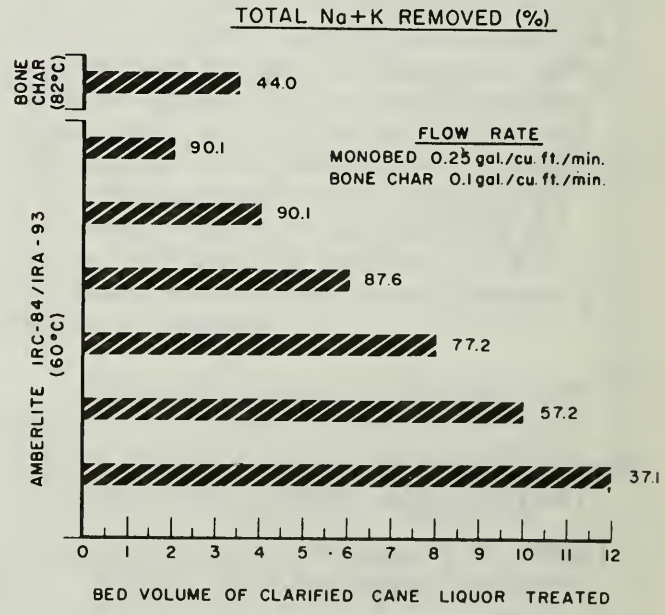

Figure 6. Comparison of total sodium plus potassium removed by ion exchange and bone char. Figures refer to percentage removed at that amount of liquor treated.

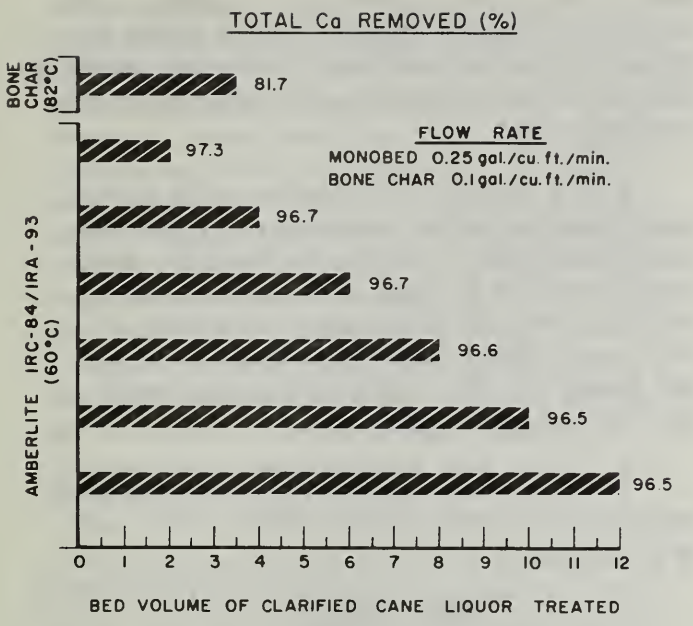

Figure 7. Comparison of calcium removed by ion exchange and bone char. The figures refer to the percentage removed at that amount of liquor treated.

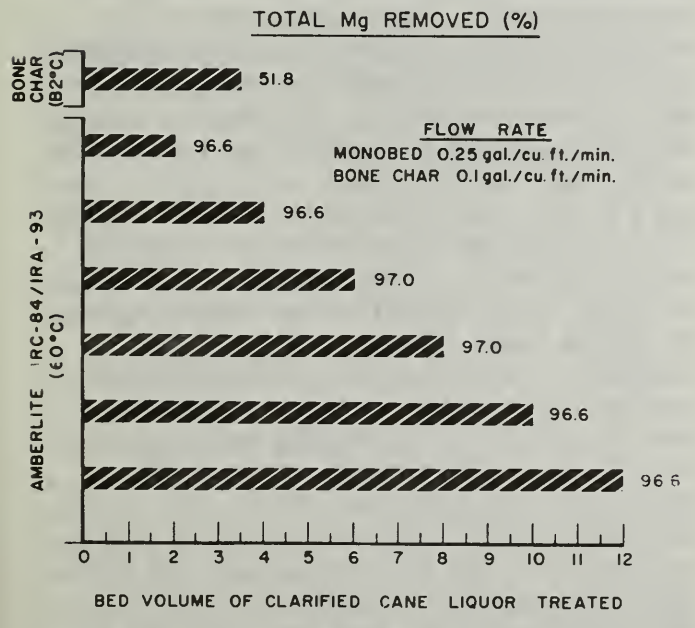

Figure 8. Comparison of magnesium removed by ion exchange and bone char. Figures refer to percentage removed at that amount of liquor treated.

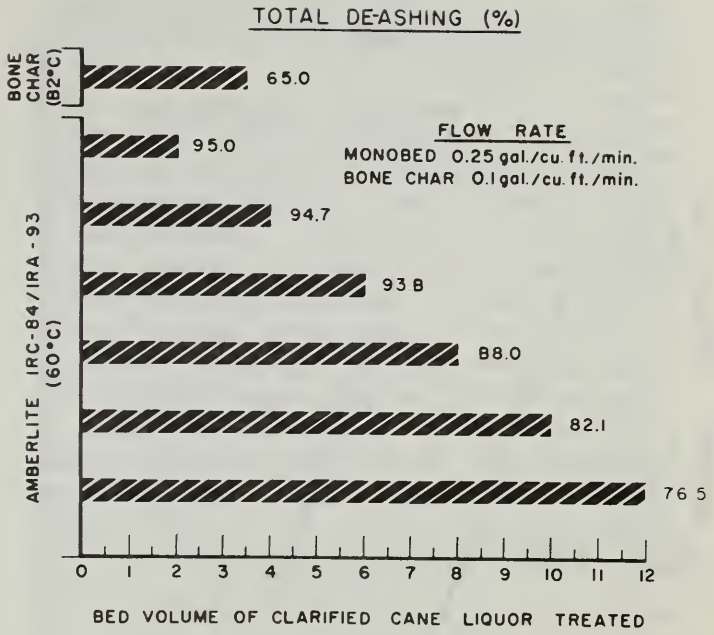

Figure 9. Comparison of total de-ashing of ion exchange and bone char. Figures refer to percentage removed at that amount of liquor treated.

the bone char or granular carbon operation for refining cane sugar syrups. Larger scale tests are, of course, required. Some approximate economical evaluation, however, may be considered. If we consider that twelve bed volumes of liquor (ca. 60 Brix) are treated per volume of Monobed per cycle, this corresponds to about 600# sugar per cubic foot per cycle. If we further consider that the major chemical cost will be the cost of the base (NH_3 or NaOH) used to regenerate the anion exchange resin, this should require no more than 1 lb. NH_3/cu. ft. or a cost of $0.03/cu. ft. which corresponds to $0.005 per 100 lb. sugar. Based upon previous experience, the overall cost of the Monobed operation should be less than $0.01/100 lb. sugar. The waste NH_3 regenerant can be recovered with an equivalent amount of lime thereby lowering the regenerant cost by at least a factor of four. This technique is used universally in the manufacture of soda ash and has been used to advantage in the beet sugar industry in France.

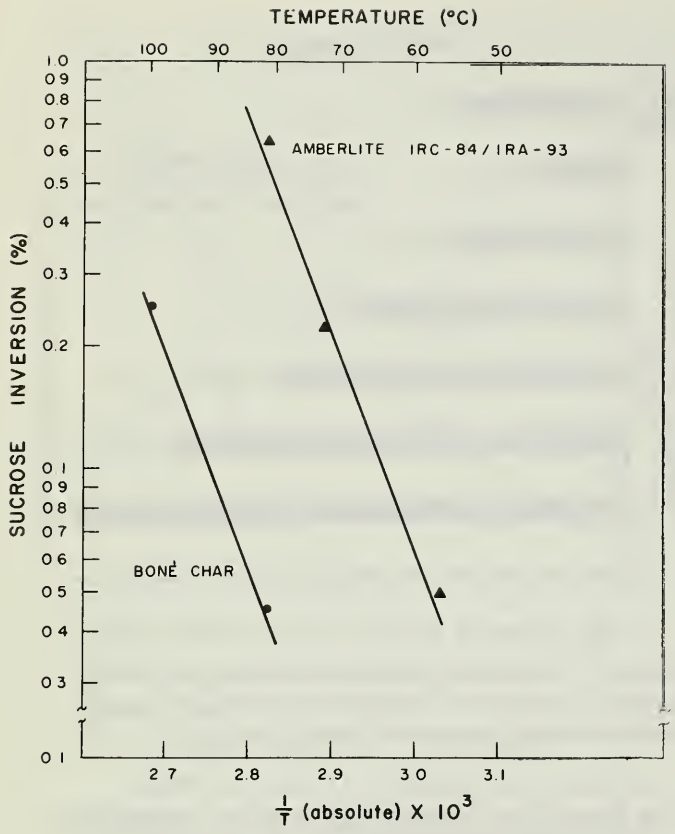

Figure 10. Inversion of sucrose by ion exchange and bone char. Ion exchange at 60° C. gives no higher inversion rate than bone char at 82° C.

Since one can operate the Monobed at flow rates considerably greater than those employed for bone char, the capital costs for the Monobed ion exchange operation should also be considerably less.

It is also of interest to consider this study in the light of the progress previously made in the use of ion exchange resins for refining cane sugar. Ion exchange resins are now employed economically for the decolorization and deionization of cane sugar syrups following either a carbon or bone char pretreatment. The new Monobed technique is merely a continuation of this progress. By merely substituting two new ion exchange resins, used extensively for water treatment and for corn and beet sugar refining, for those ion exchange resins now used for cane sugar decolorization and liquid cane syrup production, it appears that one may be able to extend the use of ion exchange resins in cane sugar refining, possibly augmenting or eliminating the use of carbons and bone char.

With respect to the regeneration of the weak electrolyte ion exchangers, it has been established that these ion exchangers can be regenerated at almost 100% theoretical or stoichiometrical efficiency with H_2SO_4 or even waste SO_2 contained in flue gases (for the Amberlite IRC-84) and NH_3 and NaOH (for the Amberlite IRA-93).

Further studies on this new ion exchange technique for refining cane sugar syrup are in progress.

DISCUSSION

L. A. Anhaiser (Imperial): From the standpoint of temperatures and sucrose concentration, are there any basic limitations to the use of ion exchange resin?

R. Kunin (Rohm and Haas): There are several limitations, of course, in the use of ion exchange resins. One must consider irreversible fouling, overall physical stability, and some of the hydraulic properties of the ion exchange materials. The physical shape, and some aspects of the physical appearance about which we have heard, are of less concern to me. One of the most difficult factors to be considered in ion exchange materials is their density. If you measure the density of ion exchange materials and measure the density of sugar syrups, you'd say you should be running upflow and not downflow because resin floats. Almost all resins float in syrups of this density and we can't expect you to dilute these syrups to the point where the resins will truly sink. The interesting thing about this is that as long as there is a hydrodynamic pull on the resin, as long as you don't stop the flow before you start sweetening off, then the resin sits at the bottom. To be quite frank, some of the early pioneers in the use of resins had a great deal of courage in trying out the process on the scale that they did. I would have

anticipated much more trouble than we now experience. From a physical point of view, the thing that bothers me most about the limitations of ion exchange is the matter of low density. I don't think that there is a thing that we can really do about it. The resin does seem to stay in the unit as long as the flow is maintained in a downflow direction. I would say that if we had to operate ion exchange at the flow rate that you use on bone char we might indeed be in trouble, from a hydraulic point of view, with floating and circulation within the bed. From a kinetic point of view we seem to have balanced it out, however, and at these flow rates the resin works satisfactorily.

F. M. Chapman (SuCrest): I think that it is important that we get our standards right. In the first of the slides, you plotted Amberlite against bone char. At the top of this curve, bone char actually showed some superiority in color removal and to keep matters in the right perspective, I must say that in a really good bone char operation we would get 10 or 20 volumes of effluent with an average decolorization of 93%.

R. Kunin: This difference in scale has been pointed out to me and I have no real answer for it. I merely wanted to get a feel for what happens on the same scale and flow rate that we were testing. Now, as I indicated to you in my review of the annals of the Bone Char Project, there are a lot of good data and a lot of bad data. As I reviewed them more recently, last Thursday and Friday, I saw values down as low as 2-1/2 and 3 and values up as high as 10 or 11 bed volumes. I have only summarized our work here. It shows that we should be able to treat roughly the same amount of syrup that you now treat. In other words, we are treating somewhere between 10 and 15 bed volumes and at a much higher flow rate than you use with char, so I will not quarrel with your point. You probably are correct but you must also appreciate the conditions under which we are evaluating these materials. I might also add that our bed depths were shallow, and the same as those employed for the ion exchange resins. Roughly what we are saying is that we seem to be able to demonstrate that we can treat at least the same amount of syrup as can char, but perhaps in almost one-tenth the time; this, to me, is of interest. Another thing: we are getting good decolorization, approximately 90%, but we are getting a lot of ash removal. The interesting thing that I find is that we have seen references to the removal of ash by bone char. It does remove some, but half of the people we talk to say they don't obtain any ash removal, and they don't seem to care whether they do get ash removal or not; however, if you take away the ash removal they do get, they complain about the loss. I don't really know whether the fact that we are getting good ash removal is of any significance or not because the syrup is very pure to begin with.

I really want to indicate we have room for improvement here, at this very early stage of our work. We now seem to be able to operate, under the conditions that you now use, to obtain a fairly high quality of material and to get almost, if not more, sugar treated. One thing which we haven't discussed as yet: if we merely follow this ion exchange system with a small bed of a strong base resin in the chloride form, with which many of you people are already familiar, then we get a tremendous further improvement in color removal with very little added cost. In summary, I don't think that we are going to fill up all of those cisterns that the sugar industry has with ion exchange resins.

G. W. Muller (Kerr-McGee): Just one comment on Frank Chapman's and your remarks. The narrow column you are using is one of the ones that many of the refineries found inefficient for column testing of char. It may be fine for resins, but that narrow diameter gives a wall effect that is certainly tremendous in char-channeling, so I am glad to hear that you are going to wider columns. Frank Chapman has written a great deal on tub or flat type columns in series, and you get more cycles through with them.

Some of the colorants removed by bone

char are not ionic in form. How do you remove them with the ion exchange adsorbents if they are not ionic?

R. Kunin: I don't know how we are removing all of these colorants, but we are removing practically all of them. It turns out that an ion-exchange material doesn't function merely in terms of exchanging one ion for another. Many of these color bodies are removed by ion-exchange materials by forces similar to those involved, say, on carbon and other adsorbents by covalent and pi-bonding forces, and the fact is that the resin does remove them without exchanging ions. But let me also say this: that, although we say these substances are non-ionic, there are very few substances found in nature that are soluble and not somewhat ionic. I would not be surprised if most of the things that we consider as being non-ionic have some ionic characteristic to them. In any case, the ion-exchange resin functions not only in terms of acid-base reactions, or exchange of one ion for another, but also by forces similar to those involved in the chars and carbon.

N. H. Smith (C&H): In connection with those last comments: non-ionic resins also adsorb considerable quantities of colorant. This supports your statement that non-ionic forces are involved.

R. Kunin: The interesting thing is that some of those so-called non-ionic resins are really slightly ionic. But it is true that there are other forces involved here.

N. H. Smith: I had another question concerning the inversion. It seems that a lot of inversion is due to localized low pH within the pores of the resin, and probably the pH was quite a bit lower than the seven that you stopped at, so I imagine that running your columns longer would not have given you increases in inversion. I wonder if you would comment on that. Further, have you run experiments where you use the anion resin first to avoid getting low pH's and if so, what does this do to decolorization?

R. Kunin: With respect to inversion, actually we are measuring the true inversion rate due to the interior structure of the resin whatever the pH of the resin is. Figure 1 is merely the titration curve of the resin.

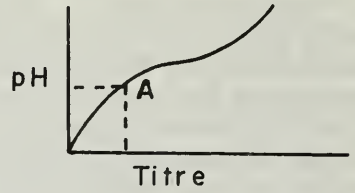

Figure 1. Titration Curve of Ion Exchange Resins.

At high pH on Figure 1 we would have practically no inversion power, while at low pH on Figure 1 we would have a considerable amount of inversion. So by partially neutralizing the resin to point A, we fix this internal pH that you are talking about by eliminating the low pH region. Actually, the pH at the time of the partial neutralization is very close to the internal pH. That is why we avoided a study with syrups containing some buffered material. The buffer would tend to neutralize the resin. We wished to establish the worst conditions that one could obtain.

E. J. Culp (American): Mr. Kunin, what do you visualize as the synthesis limits to the further development of ion exchange resins that are especially tailored for cane sugar refining?

R. Kunin: We have considerable flexibility in the design of ion exchange resins for sugar refining. I indicated to you the pore structure flexibility that we now have in handling higher and higher molecular weights that might even approach the colloidal region. I feel that we have further degrees of freedom available to us to further alter the acidity of the cation exchange material. To refer back to part of the previous question, which also relates to this question, and which I failed to answer: if we use the weak base anion resin first, the process won't function as well. In other words the weak electrolytes have to be together as a Monobed in order to function properly.

In view of this flexibility, the answer to the question on tailored ion exchange resins for sugar refining "boils down" to the amount of effort which the chemical industry, as a manufacturer or vendor of ion exchange materials, can afford to put in for the given volume of business that's available. However, all those cisterns with bone char in them are certainly justification for further experimental work.

W. R. Tuson (Colonial): Could you give us some idea of the relative cost difference between the weak base tertiary amine and the strong base quaternary amine anion resins?

R. Kunin: They are pretty close in price. They vary but slightly. The weak base resin might be a little bit less or a little more at any one time, depending upon the specific materials being compared.

W. R. Tuson: Am I correct in inferring, from your comments, that the strong base resins offer better color-removing properties than weak base resins?

R. Kunin: If you only use the resins once and throw them away, the strong base resins are the best for decolorization. I think Dr. Abrams has brought up an important point, that the weak base resins, whatever they absorb, regenerate with a much higher efficiency and a much lower tendency toward fouling. This is another reason why we are considering them here. In several current plants throughout the world, the bone char unit is used prior to a strong base anion exchange resin unit used in the chloride form for a decolorization polishing. The bone char, or carbons, are removing material that may irreversibly foul the strong base unit. In essence, the bone char is protecting a strong base anion exchange resin from fouling. Weak base anion exchange resins can function in a similar way, and this is why they are used in water treatment. Really, what we are doing here is, as has been done in water treatment and many other applications, using a weak base resin whenever we can get away with it because we can use these exchangers at a higher temperature, they regenerate more effectively, and they have a much lower tendency for irreversible fouling.

I. M. Abrams (Diamond Shamrock): Bob, we are very pleased to hear that you are thinking of applying the deionization step a little earlier in the sugar refining process. Since 1941, we have been trying to promote the idea that to get maximum benefit from deionization, one really should go all the way back to the original thin juice extract in cane sugar refining. Even partial deionization of the thin juice would be justified in that a higher yield of better quality raw sugar would be obtained. We haven't gotten very far yet, but we are still hoping.

Whenever we have tried using a combination of weak electrolyte resins, that is, a weak acid cation exchanger combined with a weak base anion exchanger, we always run into the problem which was mentioned this morning: the color precursor. Usually color precursor is associated with the nitrogenous content of the juice, and we find that the weak acid cation exchanger does not remove very much of the nitrogen. We would like very much to see a comparison between a weak acid cation exchanger and bone char in this report. I wonder if you have any data on nitrogen removal.

R. Kunin: I want to go back to the first comment. I am not going to argue with my Congressman as to import and export requirements on sugar. All I know is: you have refineries here, and they have raw cane sugar coming in and I am not going to wait for the millenium before we start doing things in the cane fields. I felt the same way as you do, some while ago, but now I feel that, perhaps, making a raw sugar first is not a bad method of refining sugar because it does an excellent job in removing troublesome impurities. Perhaps, it is more economical to go through a raw sugar in the cane growing regions, where you do not have a chemical industry built up, rather than building a chemical industry to operate in these areas, which are primarily agricultural.

Now with respect to color precursors, we find that there isn't much nitrogen in the raw sugar, and we don't have the situation, I believe, that we have with beet which is loaded with amino acids and other compounds that will give rise to browning reactions. To check the stability of our syrup, we evaporated it and found that we still had good color, and we saw white crystals coming out. I don't know whether there were any precursors here, but I do know one thing: a carboxylic acid by itself when it starts off doesn't remove much amino nitrogen, but in a Monobed it does. We found very little amino nitrogen in the syrup that goes to the bone char unit. It is a pretty pure material. I think the precursor is undoubtedly present in the raw cane sugar but I don't think we really are concerned about nitrogen in cane.

I. M. Abrams: Was there no increase in color when you concentrated the syrup?

R. Kunin: A little increase. After evaporation, it looked a little darker, of course, but when we diluted it back to the same volume, there was little visual change.

J. T. Truemper (Atlas): What was the particle size of the resin compared with that of bone char?

R. Kunin: Considerably smaller. We are dealing with the same particle size range that Mr. Moroz presented, usually a 20-50 mesh size. With this size I anticipated, to be quite frank, the hydraulic problem, but here we are not dealing with the deep beds that we normally find in the bone char and carbon. We feel that with the resins we do not need as deep a bed. The other interesting thing about this is that when you mix a weak base and a weak acid together you get a much larger particle than from either individual one. There is a little bit of a clustering effect, but basically I don't think we could ever operate an ion exchange system with the particle sizes we have, and the viscosities that we deal with, if we had to go through the number of large beds that are required for bone char. With this number of beds in series, the solution just wouldn't come through. The idea of going to much larger and larger particles is, perhaps, theoretically possible, but I don't think we'll ever see them. Since it is unlikely that we'll use larger particles, we will be limited by bed depth, but then, we don't need the depth that one requires for the char.

F. Bruder (SuCrest): As a final comment in favor of ion exchange, I might add that no one touched on sweetening off, which, with bone char, presents quite a problem in the sense that a pretty big portion of the impurities goes to the sweet water. I believe we find that in ion exchange, and perhaps in the same system that you are talking about now, the sweet waters would be relatively free of impurities. That is, the ash content and many of the nonsugars that were taken out would not come off as sweet water.

QUICK STARCH METHOD OF ANALYSIS ON RAW SUGARS

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The analysis for starch has been included in studies relating to raw sugar quality at Crockett. High starch levels might be related to slow filtration, poor color removal by char or by crystallization, or solution turbidity. This report will compare two procedures for starch analysis, the Balch and a quick method, then will review several factors which influence starch analysis.

BALCH METHOD

The method of Balch (2) was adapted for our studies and was used for several years. The detailed adaptation of the method is in Appendix 1. Briefly the procedure is as follows: Add alcohol and acid to precipitate starch along with other insolubles. Filter to catch the alcohol insolubles in a bed of kieselguhr. Wash the filter cake free of sugar and other water solubles. Digest the filter cake with boiling hot calcium chloride to redisperse the starch. Centrifuge. To an aliquot of the supernatant liquid add iodine reagent and read spectral absorbance at wavelength 700 using potato starch as a standard.

The many steps in the Balch analysis make it a day-long procedure. A more rapid method was desired, both for economies in analyst time and so that the result could be obtained more quickly.

QUICK STARCH METHOD

The first deviation from the Balch procedure was in estimating starch content of granulated sugar and liquid sugar products. Iodine reagent was added directly to the acidified sugar solution and spectral curves were run. Increases in starch level were evident for increased inboiling of syrup. The procedure was extended to apply to more highly colored solutions like filtered raw sugar crystal solutions. It was found that definite differences in level of apparent starch were observable. Testing of the analysis procedure has continued.

Appendix 2 details the current procedure for the quick starch method. In brief the procedure is as follows: to an aliquot of a clear sugar solution of known % solids add iodine-iodide reagent in standardized volume proportion and read spectral absorbance at wavelength 560. Use a suspension of amylopectin as a standard. Read the absorbance of the original solution (with acid added) to correct for the original color.

COMPARISON OF BALCH TREATMENT WITH QUICK STARCH METHOD

Having outlined the two procedures it is of interest now to look at a comparison of the Balch and "quick" methods. Various sugar samples have been analyzed by both the quick method of analysis and a modified Balch treatment. The Balch test was followed through the step of boiling with calcium chloride solution. From this point the Balch method was modified as follows. The cooled calcium chloride-starch solution was made to volume at 100 ml. in a centrifuge tube, mixed, and centrifuged to clarify. This clarified solution was then tested by the same procedure as with the quick method, i. e., 20 ml. of the clear solution was mixed with 10 ml. of the iodine reagent and 10 drops of acid, then read on the spectrophotometer at 560 nanometers using amylopectin standard calibration.

Figure 1 shows the relation between results obtained using the two procedures. Open circles are results for material which have been char filtered, e. g., No. 1 Liquor, granulated sugars and granulated syrup. For these

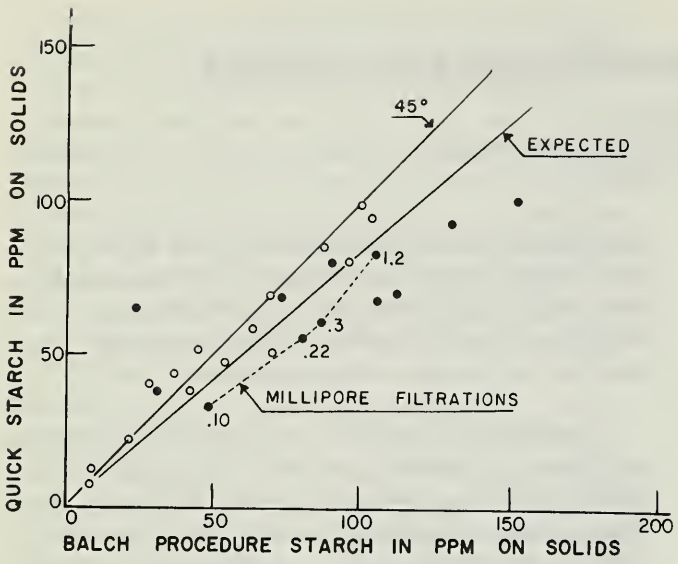

Figure 1. Comparison of Quick Starch Procedure with Balch Procedure for Starch

the correlation is quite good and is close to the 45° slope of perfect agreement, or the line of expected relationship based on adjustment for sucrose effect in the quick method, and calcium chloride effect in the Balch method. These effects will be discussed later.

Solid black circles are for filtered raw sugar crystal solutions. These points show more scatter; also there seems to be a trend for the quick starch method to give lower results than the Balch method. Four of the solid points are connected with a dashed line. These show the trend with filtration through millipores of successively smaller sizes. The number indicates the nominal pore size in microns of the millipore through which 50 Brix raw crystal sugar solution was successively passed. The nearly parallel trend line here suggests that the interfering material is well solubilized. Also, some indication of the starch particulate dimensions can be derived.

RELATION BETWEEN STARCH AND FILTERABILITY

As an example of one possible use for the results of the quick starch method, the relation between starch and filterability was looked at. Figure 2 is a scatter diagram which shows the relationship for crystal washed raw sugars as received at Crockett.

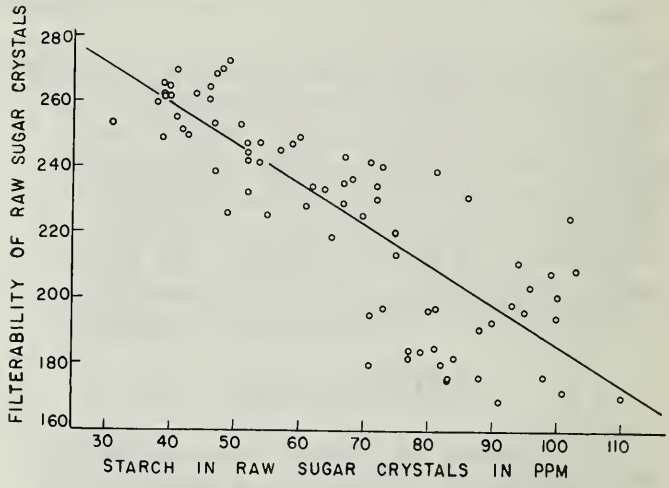

Figure 2. Comparison of Filterability of Raw Sugar Crystals with Starch Content

This subject of relationship between starch and filterability was discussed by Meads (6). The correlation coefficient for the data is -.832.

It should be noted that the relation here is between the soluble starch and the filterability. In routine quality measurement for raw sugar at Crockett a portion of raw sugar is washed down to crystal with high-purity saturated sugar solution, then alcohol. The dried raw sugar crystal is made to 50 Brix, is filtered with a standard kieselguhr under standardized conditions. The volume of filtrate collected in a specified time is designated the filterability. Routinely, the color of the filtrate is measured and calculated to crystal color. This same filtrate was then analyzed by the quick starch method under discussion.

Having shown some results of applying the quick method, it seems important to review some of the factors that are known to influence starch analysis and to relate these to the procedures used above.

STARCH STRUCTURE

"Starch" is a short word, applied frequently in household or nutritional contexts. It is important to remind ourselves that starch, although commonplace, is not simple but is complex structurally.

Most starch is generally recognized as being separable into two major classes of molecular structure (1, 3). Amylose consists of glucose units joined by 1, 4 linkages giving a linear structure. Amylopectin consists also of glucose units but is more complex in that there are a number of side linkages (1, 6 links), resulting in a branched structure. The range of molecular weights of the naturally occurring materials is generally quite broad. For amylose, molecular weights between 100, 000 and 2, 000, 000 are common. For amylopectin molecular weights have been measured in the range of 100, 000 to over 100, 000, 000 (8).

SPECTRAL ABSORPTION CHARACTERISTICS

Amylose and amylopectin both react with high concentrations of iodine-iodide reagent to give colored solutions. Amylose gives a blue color with a maximum in the absorption spectrum at a wavelength between 600 and 650 nanometers. Amylopectin gives a purple or violet color with a maximum at a wavelength between 540 and 570 nm (3). Tu and Okamoto (7) found maxima near 545 nm. for starch in Hawaiian raw sugar crystals.

The wavelength 560 nm. was chosen as standard for the starch analysis. This is close to the maximum in the spectral curve for both the sugars and for amylopectin used as a standard. The Beckman sugar colorimeter is equipped with a 560 nm. filter and might be used for this analysis. Actually, most of our analyses were performed with a Bausch and Lomb Spectronic 505 Recording Spectrophotometer so that the shape of the curves could be noted.

IODINE REAGENT

The reagent for the quick method is a mixture of iodate with excess iodide. When acidified, iodine forms, then complexes with iodide to give triiodide ion with two major absorption peaks in the ultraviolet. The ratio of iodide to iodate was adjusted fairly high to give the maximum absorption at 560 nm. for sugar samples. Absorption was higher for higher reagent concentration; the concentration and proportion of iodine reagent chosen results in an absorptivity for amylopectin about 70% of the value which it approaches asymptotically with high iodine concentration. McCready (5) discussed this technique as applied to analysis of peas. Cashen and Friloux (4) applied the technique to cane samples and reported % amylose on starch between 20 and 55%. One trial analysis of this type applied to a Hawaiian raw sugar gave us 30% amylose on starch.

One complication appears in that the variation of absorbance with wavelength does not seem to match that expected from a mixture of amylose and amylopectin obtained from potato starch. This suggests that cane starch may be different in structure. It appears desirable to investigate further this procedure for estimating amylose proportion.

At the low iodine concentrations, because of competition for the iodine, interferences are more marked. With low iodine concentrations, absorption due to amylose is much diminished in presence of sugar impurities. Therefore, to test for amylose with low iodine concentrations it is necessary to make a separation as in the Balch procedure. Other effects like the salt effect may also be much different for low iodine concentrations. Thus, it appears that the dispersing technique should be standard for both amylose and amylopectin used as references and for unknowns.

REFERENCE STANDARD

It seemed desirable to have a reference standard in liquid form. Amylopectin, avail-

able as a powder from Nutritional Biochemicals Company, was used to prepare a suspension according to the procedure outlined in Appendix 2. The spectral curve for the amylopectin-iodine complex was close to that for sugar solutions. This suspension settled slowly so it was necessary to stir well before pipetting an aliquot.

Solubility of starch is a definite problem in preparing a stable standard. It may be that the use of calcium chloride and acetic acid, as in the Balch method, would be better; even this did not disperse the amylose we had. Lithium chloride at 13 molar was sufficient. Dimethyl sulfoxide is known to be a good solvent for starch. However, DMSO was found to have an effect on absorbancy when a low iodine concentration was used (. 075 times the standard reagent concentration given in Appendix 2).

EFFECT OF SUCROSE

Since the absorbance of the starch-iodine complex is measured in the impure sugar solution it is pertinent to inquire what is the effect of the sugar and other impurities.

First the sucrose effect was studied independent of amylopectin. A starch-free granulated sugar was dissolved to 66 Brix with distilled water. The curve for iodine absorption of this sample was run against reagent blank. The relative absorption was near zero from 640 to 540 nm., dropped slightly negative with maximum negative difference at wavelength 490 nm., then climbed steeply with absorbance reading at about wavelength 410 nm. Using lower sucrose concentrations it was shown that this steep climb in absorbance is part of an enhancement of the triiodide reagent peak which normally occurs at 350 nm. wavelength. The reduction in absorbance near wavelength 500 nm. is evident in analysis of low starch, high purity sugars using a 5 or 10 centimeter cell length.

The effect of sucrose on the amylopectin absorption in the quick method was also investigated. A granulated sugar containing essentially zero starch was made to 66° Brix. Successive dilutions were made with distilled water. Into each of several 100 ml. volumetric flasks 10 ml. of 1000 p. p. m. amylopectin (prepared as described in Appendix 2) was pipetted and the flasks were made to volume, each with a different dilution of the sugar. The final solution was diluted with water alone. Table 1 gives the apparent error in amylopectin analysis as a function of Brix for both 560 and 640 nm.

The sucrose shows a measurable but small depressing effect on the amylopectin absorption at 560 nm., and a considerably larger depression of readings as measured at 640 nm.

Other tests demonstrated that Beer's law was closely obeyed as the amylopectin was diluted while keeping the sucrose concentration constant.

IONIC EFFECTS

The literature reports that the ionic content affects the spectral absorption of the amylopectin-iodine complex. The effect of sodium and calcium chlorides on amylopectin-iodine absorption at 560 nm. was tested by experiments similar to those discussed for sucrose. Results are shown in Table 2. Errors were measured for 100 p. p. m. amylopectin. The salt concentration refers to the solution taken for test before adding the reagent.

Table 1. --Effect of Sucrose Concentration on Iodine Absorption, Amylopectin, 100 p. p. m. on Volume

RDS of Sample Before Mixing of Reagents	% Error Due to Sucrose at Wavelength	
	560 nm.	640 nm.
0	0	0
15	-0. 6	-3. 2
30	-1. 6	-7. 1
50	-3. 4	-13. 6
70	-6. 4	-20. 7

Table 2. --Effect of Salts on Iodine Absorption Wavelength 560 nm.

Salt Concentration in gms/100 ml for Sample Before Mixing with Reagent	% Error Sodium Chloride	% Error Calcium Chloride
1	+5.1	+9.6
2	+8.0	+11.3
4	+10.2	+13.0
8	+12.6	+15.9

CONCLUSION

The quick starch method appears to be a useful and meaningful procedure, especially when applied to granulated sugars and similar char-filtered products.

For refinery process liquors closer to the raw sugar end there is evidence that interferences may occur. It may be desirable to study the nature of these interferences further. Nevertheless there is a place for the quick starch procedure as a quickly obtainable criterion of quality; or the method may be applied for a quick check on the effect of some process treatment.

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APPENDIX 1

STARCH DETERMINATION IN SUGARS

R. T. Balch, The Sugar Journal, 15, 11-15 (Jan. 1953)

1. Weigh out 50 grams of raw sugar (see footnote) and dissolve in 50 ml. of water.

2. Add 10 ml. of 1N HCl and 150 ml. absolute or 97% denatured EtOH. Allow to stand one hour.

3. Add 1.5 grams diatomaceous earth filter aid (Celite Lab Grade) and filter the mixture through Whatman No. 1 paper fitted in a small Hirsch funnel and precoated with 0.5 grams of the same filter aid.

4. Wash the cake thoroughly with 150 ml. of 70% EtOH followed by 60 ml. of hot abs. EtOH and 60 ml. of hot acetone.

5. Transfer the cake to a 250 ml. beaker, add 20 ml. of the neutralized (use NaOH or HCl as required) $CaCl_2$ solution (sp. gr. 1.3, 62.3° Bx) 5 ml. of 0.5% acetic acid and 40 ml. distilled H_2O and mix thoroughly.

6. Cover and heat the mixture to boiling and continue gentle boil for 18 minutes.

7. Transfer the contents of the beaker to a 100 ml. calibrated centrifuge tube, quantitatively, with water.

8. Make up to mark after cooling to room temperature and add 1 ml. of water extra to compensate for the volume of filter aid. After making to 101 ml. mix contents by inverting tube several times.

9. Centrifuge out insoluble matter at about 2000 r.p.m. for 10 minutes or until the supernatant solution is clear.

10. After centrifuging 10 minutes pipette at least 75 ml. of supernatant solution into another tube and centrifuge again for 10 minutes.

11. Transfer an aliquot (see footnote) of the clear solution, containing from about 0.5 to 2.0 mg. of starch, to a 100 ml. volumetric flask and dilute to about 75 ml. with water.

12. Add in sequence, 5 ml. of 10% acetic acid, 1 ml. of 10% KI and 10 ml. of 0.01 N KIO_3 (0.1785 grams per 500 ml.) for color development.

13. Make up to 100 ml. with distilled water, mix contents and measure the color at 700 nm. against a blank solution containing the same chemicals and amounts.

14. Translate the transmission reading on the unknown in terms of mg. of starch from data obtained by the analysis of known amounts of starch conducted in the same manner (see footnote). Use C. P. potato starch as standard.

15. Calculation

$$\text{ppm starch} = \frac{(10^6)(-\log T \text{ sugar})(\text{starch aliquot})(\text{g. starch})}{(-\log T \text{ starch})(\text{sugar aliquot})(\text{g. sugar})}$$

Footnote: Amounts used for various starch analysis in steps 1 and 10.

Raw Sugar & Washed Raw	10 ml. Aliquot
Weigh 50 grams of the sugar	and dissolve in 50 ml. of water
White Sugars	70 ml. Aliquot
50 g. of sugar and 50 ml. water	
Liquors	
75 g. liquor and 25 ml. of water	

Amount of Starch in Standard - 0.0200 grams

APPENDIX 2

CURRENT PROCEDURE FOR STARCH ANALYSIS IN PROCESS MATERIALS

(Tentative, Apr. 1967)

General

This procedure is applicable for clarified process liquors and for granulated sugars. Its purpose is to give a rapid estimate of starch for possible use in control of sugar quality.

All pipetting should be done with rubber bulb to obviate the possibility of contamination with enzymes from the saliva which might hydrolyze the starch.

Amylopectin is used as the standard since its wavelength of maximum absorption matches closely those observed for the starch found in most processing samples.

Preparation of Standard Amylopectin

Weigh out 500 mg. of amylopectin. Transfer to 250 ml. Erlenmeyer flask, rinsing weighing dish into flask with not more than 10 ml. of ethanol. Disperse in flask. Add 50 ml. of one normal NaOH. Heat to boiling with continuous stirring. Boil about 15 minutes. Cool. Add 50 ml. of normal HCl. Cool, transfer to 500 ml. volumetric flask and make to volume with saturated benzoic acid.

This solution contains a nominal 0.1% or 1000 p.p.m. of amylopectin. Prepare one or more dilutions of the above stock solution using saturated benzoic acid. The usual nominal dilutions are 50 p.p.m. and 5 p.p.m. Before any pipetting of amylopectin standard shake the bottle vigorously to resuspend all material that has settled out.

Apply a correction to the nominal concentration for moisture in the amylopectin as determined by drying overnight at 70° C. in a vacuum oven. For example, if moisture in starch is 12.5% then the amylopectin is reduced by the factor .875; a nominal 50 p.p.m. is 43.8 p.p.m. amylopectin.

Preparation of Reagent

Prepare stock solutions to concentrations shown below; into a 500 ml. volumetric flask, pipet 25 ml. of each of the stock solutions.

Stock Solution

Potassium Iodide (30 g./Liter)
Potassium Iodate (2.14 g./Liter)

Make to volume with distilled water. Mix. Filter. Store in a glass stoppered bottle.

Analysis

For raw crystal samples and process liquors having between 10 and 150 p.p.m. starch on solids

A. Into a 125 ml. Erlenmeyer flask measure the following:

20 ml. of sugar solution
10 ml. of iodine reagent
10 drops of 75% phosphoric acid
Swirl to mix.

NOTES:

1. It is convenient and generally sufficiently accurate to measure sugar liquor and reagent in fast flowing pipets and to read the mixture in a 1 cm. cell.
2. When volume of starch containing solution is limited the volumes can be reduced in proportion even down to 2 ml. of starch-containing unknown solution. In this case mixing can be done in the 1 cm. cell. This procedure can be applied for small volume effluent fractions in gel permeation chromatography.

B. Read absorption on a colorimeter or spectrophotometer at 560 nm. As a reference use a blank prepared from water in place of the sugar solution. Blank in reference cell should be covered to keep oxygen out. Solution should be read as soon as possible after mixing.

Run standard amylopectin in the same way to prepare a calibration line or factor relating p. p. m. amylopectin and absorbance.

For colored solutions it is necessary to correct for the measurable absorbance at 560 nm. Rinse the cell with the sugar solution; then, fill with original sugar solution, add one drop of phosphoric acid for each 3 ml. of cell volume and mix in cell. Read at 560 nm. using water as the reference.

Correct the observed iodine absorption at 560 nm. for the sample by subtracting 2/3 of the sugar solution color absorption at 560 nm.

Analysis for Production Samples of Granulated Sugars or Liquid Sugars Having 0 to 20 p. p. m. Starch on Solids

Into a 200 ml. Erlenmeyer flask add 50 ml. of sugar solution from a graduated cylinder. Measure 25 ml. of reagent using a graduate. If the sample is a viscous liquid rinse it from the 50 ml. graduate into the flask with the reagent. Add 25 drops of phosphoric acid.

Read absorption at 560 nm. in 5 cm. cells against reference prepared from water instead of sugar solution. For color-turbidity correction mix 50 ml. of sugar solution with 25 ml. of water; correct the iodine absorption with the full value of the 560 nm. absorption for this solution.

Calculation of Results

A sample calculation is shown below. All absorbances are multiplied by 1000.

Calculate the factor in this way:

$$\text{Factor} = \frac{\text{p.p.m. Amylopectin in Standard}}{\text{Absorbance of Standard Solution}} = \frac{43.8}{370} = .118$$

Calculate for each sample as follows:

Absorbance of sugar solution with phosphoric acid, no reagent	= 90
Color correction to iodine absorbance = 90 x 2/3	= 60
Absorbance of Reagent-Sample mix	= 400
Color-corrected absorbance = 400 - 60	= 340
Multiply by factor 43.8/370 = .118	= 40.2 p.p.m. by volume
Multiply by solids correction factor. A function of Refractometer Solids	For 50 Brix x 1.626
% Apparent amylopectin on solids	= 65.5

DISCUSSION

W. L. Reed (Revere): I would like to ask about the reproducibility or the stability of the measurements. We have been interested in starch, since we are getting involved with more and more of the different types of world raw sugars than previously, and realize how long the regular modified Balch method takes. If you were to follow your proposed procedure exactly, and then redo the same sample, would you get good reproducibility? The errors in the correlation that you show between the two methods could be due to some unexplained items, or it could be due to errors in the method itself.

D. F. Charles (C&H): We haven't really made much of a study of reproducibility. We were happy to show that we did have differences from one sugar to another, and these did seem to relate to the sources of the sugar, as well as to other characteristics like the filterability. Are you thinking in terms of the fact that the Balch method itself may give you poor reproducibility?

W. L. Reed: That is one of the points. Another is that earlier this year, through some kind of an accident, something happened to the pH of one of our reagents--I think it was the calcium chloride--and we got a set of bad results. When the lab men investigated, they decided that we should put an extra requirement into our method to be sure the same mistake didn't happen again. This ties in with what you said about the necessity for pretty dependable concentrations and operating conditions to prevent considerable variation. I don't think we worry about a couple of parts per million on the starch. Your's seems like a very good method. Would you say it had a roughly equivalent reproducibility to the Balch method?

D. F. Charles: Well, I would hesitate to say. Actually, it may depend on how long you let the sample stand. If the sample is allowed to wait overnight and the analysis is then repeated, degradation of the starch may have occurred. I don't think it has happened in as short a time as overnight, in our experience, but we have had cases where we thought that we would just put a sample away and analyze it later and so put it in the refrigerator and, maybe a week later, went back to it. Analysis in some of these cases produced different results. Presumably this may have been due to bacteria or yeast, which produced an enzyme which may have been eating at the starch. In fact, we got one poor result where we had some stuff left in the refrigerator, and instead of having a maximum of absorption at 560 nm., we got a maximum up at 600 nm., as for amylose. This I have not explained. Another possibility for error here is contamination by saliva during pipetting, since saliva, of course, contains starch-degrading enzymes. I really can't make a definite statement on the matter of reproducibility.

W. L. Reed: Apparently the procedure is still somewhat in the development stage but it seems like an excellent idea. We are very pleased.

W. R. Tuson (Colonial, U. S. A.): Is there any chance of an entirely new method for starch--not employing iodine or iodate?

D. F. Charles: In "Methods in Carbohydrate Chemistry," Vol. IV, p. 170, Carroll and Cheung discuss Congo Red, which complexes with starch, presumably such as iodine does. Their literature citation in J. Phys. Chem. refers also to methylene blue. I might mention also that corn starch researchers have studied the reaction between iodine and starch, in terms of potentiometric and amperometric titrations, and they find characteristic differences between amylose and amylopectin, and between different types of starch. This is using iodine but measuring it in a different way. It may well be that something else entirely new will come out one of these days.

C. W. Davis (Colonial, Australia): I noticed on Figure 2 that you showed a reduction of starch, from 110 down to about 30 parts per million, and a concurrent improvement in

the filterability figure. I wonder if you could tell us what that represents to the refinery. In other words, what a drop of 80 parts per million of starch in the raw crystal will mean to the refinery?

D. F. Charles: Referring to Figure 2, a change from 100 p. p. m. to 40 p. p. m. corresponds to a change in filterability from 190 to 260. For a statement of how this relates to refinery filtration rates I would like to refer you to Phil Meads.

P. F. Meads (C&H): I think that this is more properly an item that we should take up tomorrow afternoon when we discuss raw sugar quality. I think it is fair, however, to remark that the filterability numbers given by Mr. Charles are different than those used in the Number 10 Contract. This is a filterability test used in the Hawaiian sugar industry. I was planning to mention this tomorrow. However, filterabilities of 260 represent very good filtering sugars; those at 180 are, I'd say, fair filtering sugars: these are not poor filtering sugars. I think we ought to discuss this more tomorrow.

C. W. Davis: Thank you. I am quite aware that this is properly for tomorrow, but my curiosity overcame me. One question of major importance in starch tests seems to be the solubilizing of the starch. Now, I wasn't quite clear from the early discussion as to what happened. I understood you to say the solution was filtered in conducting the filterability test. The starch, of course, was done on the crystal sugar before filtration and not on the filtrate, I presume.

D. F. Charles: No! The starch analysis test was done on the clear filtered liquor after passing a good filtration with standardized Kieselguhr.

C. W. Davis: I don't quite understand. You do a filtration test. You filter the dissolved crystal through a Celite filter aid.

D. F. Charles: That's right. Perhaps this isn't starch. However, this is material that is soluble, if you like. Just why I am not sure. Presumably it is complexed with salts of some sort.

C. W. Davis: You mean the starch test was done on the filtrate from the filterability test?

D. F. Charles: Yes.

C. W. Davis: I am sorry but you astound me. I guess that I have run out of questions now.

R. Kunin (Rohm & Haas): This may sound a little ridiculous, but have you tried a separation of the sucrose and ash by some technique employing one of the Sephadex materials which can be employed for the separation of solutes on a high molecular weight basis?

D. F. Charles: We haven't done specifically the type of thing you are asking about. We did use Sephadex A200, designed for the high molecular weight materials, and we found that the material which causes a reaction with iodine was in part excluded and in part distributed, suggesting a high and broadly distributed molecular weight. In a sense, at that point, we had made a separation. On the other hand we didn't do this as a quantitative test. We were getting such low results, because of dilution and low initial concentration, that it was hardly possible to answer the question of the cause of the interference.

R. Kunin: The reason I ask is that, routinely, with no more dilution than a factor of one or two, one can eliminate the interference of the sucrose and ash.

D. F. Charles: It might be a desirable procedure. Thank you.

THIRD SESSION: R. S. Patterson, California and Hawaiian Sugar Co., Chairman

SEPARATION OF COLORANTS FROM CANE SUGAR

Leon Farber, E. J. McDonald, and F. G. Carpenter
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INTRODUCTION

The identification of the sugar colorant has proven to be a most difficult task. Although we know it is there because we can see it, it is a most elusive and fragile substance, present in extremely small quantities, and most difficult to separate from all the sugar. Sugar chemists for years have employed all manner of ingenious methods for separating and characterizing the colorant, but there has always remained in the background those disconcerting thoughts that perhaps the material they obtained was not the same as that originally present in the sugar, and perhaps it was only an insignificant part of the total colorant. High voltage paper electrophoresis as developed by Gross (1) makes it possible to provide some answer to these perplexing questions. Gross pushed Paper Electrophoresis (PE) to its logical limit and as it is practiced today (2) it has given sugar chemists their most powerful analytical tool for the separation of sugars, sugar derivatives, sugar constituents, and sugar colorants. PE can easily separate the sugar colorant into more than 20 fractions that can be discerned either visually, by sprays, or by ultra violet (UV) fluorescence (3). PE like paper chromatography is limited to small amounts and its quantitative aspect is little better than order of magnitude at best. It is, therefore, poorly suited for preparative scale separations. It can only give some indication of quantitative amounts, but without doubt it is ideally suited for monitoring other separations.

Now in any chromatographic type separation giving a very large number of peaks or spots, there is always a problem of identifying the same spot on different chromatograms. The motion relative to a standard, while helpful, is somewhat dependent upon amount, and serious overloading of even a spot quite far removed can very greatly alter relative movement (M values). It would therefore be advantageous to have an additional criterion for identification of the spots.

In the course of many electrophoresis runs on sugar colorants, one slowly gets to recognize certain spots by their (a) visual color, (b) fluorescent color, and (c) relative motion. No one of these characteristics alone is sufficient for positive identification, but collectively they leave very little in doubt. We have instituted an arbitrary catalogue of spot numbers covering the range of substances found in cane juice (which is the starting material). The appearance of these spots is described in sufficient detail so that other investigators should be able to unequivocally find the same spot in their laboratory, a feat which, although long desired (4) has not up until now been accomplished with certainty. These spot numbers allow us to follow the individual colorants through the processing, and to identify a colorant that has been extracted, or separated by some other means, as the same that appears in the commercial process, and even to get some idea of the relative amounts.

Some of the spots that appear throughout the process have been chosen for separation in larger amounts and eventually complete identification. The results of various extraction systems are discussed and one spot has been partially identified.

ELECTROPHORESIS OF SUGAR COLORANTS

The electrophoresis for all the work described here was done in borate buffer. This system is the one usually arrived at by persons working in sugars (5, 1, 6).

Specifically the conditions are:

Paper: Whatman 3MM, 70x23 cm. (27-1/2 x 9 in.) (Narrower strips are often used)
Temp.: 15 ± 1° C.
Buffer: 0.05 molar sodium tetraborate (borax)
pH: 9.2
Voltage gradient: about 100 volts/cm.
Time: 20-100 min. usually 45 min.

Equipment:
After Gross (2), water cooled plates 54x33 cm. pneumatically pressed against the paper for close contact and good heat transfer, using 0.5mm. (0.020 inch) thick polyethylene sheets for electrical insulation. Power supply capable of 10 KV at 0.5 amp. DC. Only minimal line frequency filtering required.

The sample was applied along a pencil line about 1/3 of the length of the plates from the negative end. The applicators were made from capillary melting point tubes (1.6-1.8 mm. OD) drawn down to about 0.3 mm. OD. The sample was applied sometimes as spots but usually as a streak about 20 mm. long. Getting the right amount on the paper takes skill. After the sample had dried on the paper, the paper was dipped in buffer to within 5 mm. (1/4 inch) of the sample area and blotted lightly. (Amount of blotting was not critical). The other end of the paper was then wetted with buffer as above. The paper was placed in the press between the electrical insulating sheets. After the buffer had flowed into the sample area by capillarity and the entire sheet was wetted (1 min.) the voltage was applied for the required time. After the electrophoretic separation was complete and the paper dried, several visible yellow and brown regions could be detected, as described by Gross (2). However, if the paper were viewed under UV light* then a great many fluorescent bands become vividly apparent. There are two readily available high intensity UV light sources corresponding to the very strong mercury arc wavelengths of 253 nm. and 365 nm. These two sources produce different fluorescence in some of the sugar colorants and these differences may be used to help identify them.

A complete study of the fluorescence of sugar colorants using a spectrophotofluorometer is definitely indicated, but is beyond the scope of this paper.

FLUORESCENCE PHOTOGRAPHY

Because the sugar colorants as separated by electrophoresis are not stable on the paper for more than a few days, if a record is to be kept, then the chromatogram must be copied, traced, photostated, or photographed, for a permanent record. The speed of the Polaroid system of photography makes it ideal for this purpose. Photography of fluorescence, however, requires some unusual arrangements. The silver halide emulsion of photographic film is extremely sensitive to the UV wavelengths of the exciting source and pictures taken without any filtration will reveal mostly the exciting source wavelengths and little or no fluorescence. Figure 1 shows that photographic prob-

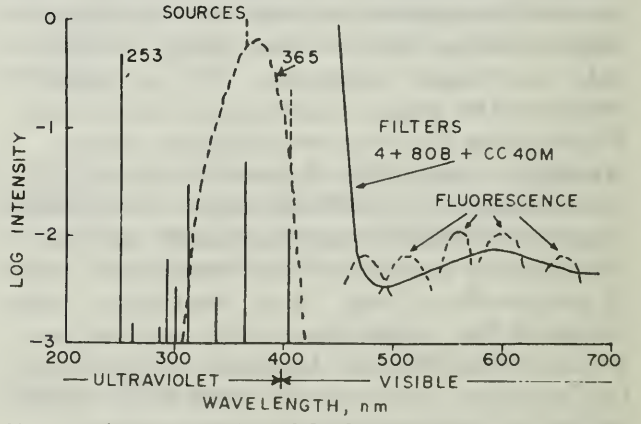


Figure 1. Intensity of light sources and fluorescence showing cut off point of filters used for photography. FGC-1-144

*By use of such as the Chromato Vue cabinet, Ultra Violet Products Co., San Gabriel, Calif.

lem. Both UV sources are really low pressure mercury arcs operating in the usual fluorescent lamp fixture. The far UV source (253 nm.) is a germicidal lamp which is designed to maximize the 253 nm. wavelength and is in a quartz tube for transmission of this wavelength to the outside of the tube. This light is filtered through a far UV transmitting filter (Corning Glass No. 9863) to remove the visible portion of the light. The result is as shown in Figure 1 and consists of a line spectrum in which the 253 line is 10 times more intense (one unit on a log scale), than any of the other lines.

The near UV source is again a mercury arc but with a phosphor on the inside of the tube which absorbs the 253 nm. wavelength and fluoresces at a wavelength near 365 nm. This gives a continuous spectrum as shown as a dashed line in Figure 1 but with the peaks of the mercury lines at 365 and 405 sticking out above the continuum. The tube itself is made of a UV-transmitting, visible-absorbing glass such as Corning No. 5874 so no further filtration is needed even though some units do use additional filters.

Note that the peak intensity of the 365 source is about 0.3 log units, or a factor of 2, more intense than the 253 source. The energy is proportional to the intensity squared, so the 365 source contains about 4 times the energy of the 253 source. However, the 253 source is in most cases involving sugar colorants a far more efficient producer of fluorescence so that the photo exposure is only about half of that required when using the 365 source.

The fluorescence from sugar colorants is about 100 times (2 log units) less intense than the exciting radiation and displaced from it toward the longer wavelengths as shown in Figure 1.

For visual observation of the fluorescence, the eyes are insensitive to the UV radiation, and only little sensitive to the blue. Therefore, a mental correction can be made for the slight bluish cast over everything and no filter is needed at all except for safety in removing the very intense UV which could cause severe sunburn. There are many UV filters of clear or very faintly yellowish glasses and plastics that will do that.

For photography, the fluorescence is separated from the exciting wavelengths by means of a UV-absorbing visible-transmitting filter that cuts off just above the 436 nm. mercury line. The Kodak Wratten Filter No. 4, which cuts off at 450 nm., was found to be most suitable as shown in Figure 1. This filter is placed over the camera lens.

The very common K2 photographic filter (Wratten Filter No. 8) cuts off less sharply at 470 nm. and is suitable for black and white photography but distorts the colors too much toward the yellow for color photography. In color photography, the No. 4 filter that was used to cut out the exciting wavelength also cuts out some of the blue. This can be corrected by adding a Wratten No. 80B filter (blue) which slightly enhances the blue. Also, the fluorescence toward the longer wavelengths, or red, tends to be a little weaker, so an additional color correction filter No. CC40M (magenta) was also added to enhance the red. The purpose was to obtain better contrast rather than to obtain a more true to visual appearance photograph.

The film also makes a difference. In the Polaroid system only one color film is available, which gives poor contrast and colors, but it is better than black and white and you do get your print right away. In 35 mm. or slide photography, Ektachrome X film was found to produce the best contrast and hence the most informative photographs, and they were not far from agreement with visual appearance.

Using two 20 watt tubes in the source, a fluorescent intensity through all the filters of the order of 0.01 foot candles was observed, requiring an exposure of the order of 2 minutes at f/5.6 with the above color films.

The differences between the two exciting wavelengths can best be emphasized by having the two photographs directly adjacent to each other. This was most easily accomplished by double exposure. One half the paper was covered by a piece of heavy sheet metal painted a flat black, and the exposure made with one light source. Then the other half of the paper was covered and exposure made on the same film with the other light source.

The photographs of this report show the Fluorescence obtained from Ultraviolet excitation of the high voltage Paper ElectrophoreGram (FUPEG) as described above. In all photographs the origin is on the right and motion was toward the plus electrode on the left. The black spot or spots appearing toward the left are the picric acid marker (see below). Unless otherwise noted, the upper half of each trace was excited by UV light of 253 nm. wavelength and the bottom half by UV light of 365 nm. wavelength.

RELATIVE MOBILITY OF THE SPOTS

The relative motion is usually used to identify spots in chromatography but it is well known to lack precision. In the presence of a great many spots, which is the case for sugar colorant, this lack of precision can be great enough for the position of a spot to overlap 2 or 3 others which makes identification questionable at best. Some improvement can be obtained by making the separations always at strictly standardized conditions (4); however, standardized conditions imply a particular instrument which may not be conveniently duplicated in another laboratory.

In measuring relative motion, one must choose a standard to measure the motion relative to. It has been the practice in this laboratory for many years to use hydroxymethylfurfural (HMF) (a sucrose degradation product that is sometimes present anyway) as the zero mobility marker. It is colorless itself but can be detected by sprays for sugars and also by ultraviolet light of short wavelength.

The ideal zero mobility marker has not yet been found. It should be soluble in water, have no net charge at all pH to achieve zero mobility, not be adsorbed to the cellulose of the paper, not react or complex with the buffer (Borate), and be brightly colored. Caffein (6) and sucrose (4) have also been used but we find that sucrose does move a little.

We have followed the suggestion of Gross (4) and are now using picric acid for the mobility standard. It is brightly yellow colored, has no adverse reactions, and moves about midway among the sugar colorants.

EFFECT OF SUGARS

One of the other problems in sugar colorants is the separation of the colorant from all the sugar. Since this separation is often incomplete, there is commonly some sugar with the colorant. In trying to apply enough material to the paper to be able to see the colorant, the paper can easily be overloaded with sugar. This causes variation in the relative motion.

The sucrose moves in the opposite direction from the colorants and so is soon out of the way, but the invert sugar components move about midway among the colorants and so are very much in the way.

This effect was amply demonstrated in the following experiment:

A sample of sugar colorants containing little or no invert sugar was applied in equal quantity to the same paper in four short streaks. One was left as it was (Top in Figure 2); to the others were added increasing amounts (in the ratio of 1:2:4) of an inverted pure sucrose syrup. (The proper amount was determined by trial). Two spots of the marker were placed on each streak. The results are shown in Figure 2 as the fluorescence from the 365 nm. source. The starting points are marked as the double vertical line right of center. The zero

mobility marker (HMF) appeared at the points marked O. (Anisidine spray was used on this end of the paper to bring out the HMF and it also shows some uninverted sucrose). The picric acid mobility marker appears black because it quenches the fluorescence of the paper. These points are marked +. Two prominent bands are marked with dotted lines on each streak, and the numbers written in are the mobilities relative to picric acid and HMF. Note that with increasing amounts of invert the mobilities decrease. In the extreme case, the mobility that was originally 0.71 was reduced to 0.40 and overlaps the other band that was originally 0.41.

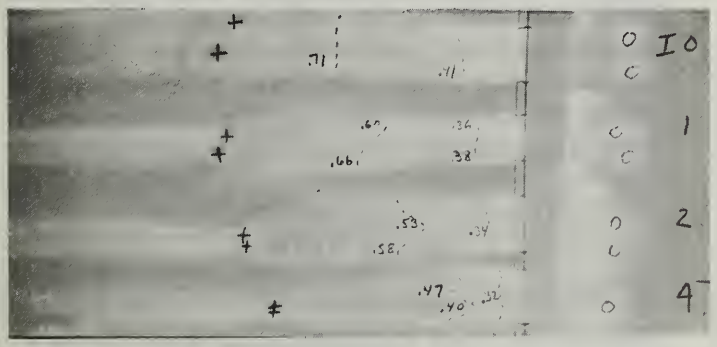


Figure 2. FUPEG showing effect of invert sugars on mobility of sugar colorants. Fluorescence from 365 nm. excitation. FGC1-137

In addition, the advance becomes irregular and the streak is narrowed just beyond the point of picric acid, marked +. The invert sugars, glucose and fructose, move just a little less than the picric acid and are at the point where the streak widens. Evidently, the sugars are of sufficient concentration to upset the even ionic strength, pH, and electrical conductivity of the buffer. This results in a distorted voltage gradient with lateral components and produces uneven advance, a condition that might properly be called overloading. The net result is to make mobilities a poor criterion for identification of the color bands if there is any possibility of overloading with invert sugars. It is also quite possible that the paper could become overloaded with any of the colorant bands, which would again cause variation among nearby mobilities. In practice a mobility variation of ± 5% is often encountered.

PREPARATION OF CANE PIGMENTS

The object in preparing a material containing cane pigments was to obtain the widest variety of cane pigments in approximately equal concentration with a minimum of sugar. No attempt was made to obtain all the cane pigments or even a representative sample. All that was wanted was a wide variety that could be catalogued. The procedure was as follows:

Stalks of sugarcane were cut with a power saw into 1 inch lengths. The center pith containing the sugar was cut out with a cork borer, leaving thin cylinders of rind. These cylinders were cut lengthwise with a knife into many narrow strips about 1/4 inch wide, 1/8 inch thick and 1 inch long. These were covered with water in a stainless steel bucket, brought to a boil and simmered for 15 minutes. They were then pressed in a Carver Laboratory press at about 2000 p. s. i. The solution was discarded and the solid pieces of cane rind retained. The rind was again covered with water, brought to a boil and pressed out, the object being to wash out most of the sugar. The third time, the rind was covered with water, brought to a boil, but this time only drained to obtain a colorant rich solution containing very little sugar. This solution was evaporated to the extent that 100 g. of cane rind yielded about 5 ml. of final solution which was then spotted on the electrophoresis paper.

FLUORESCENT SPOT NUMBERS

The electrophoresis was run for different lengths of time ranging from 25 minutes to 100 minutes to spread out the colorants to different extents. The results are shown in Figure 3. This picture is an Ektacolor print made from an Ektachrome X transparency obtained as described under Fluorescence Photography. Figure 4 directly below is a black and white Polaroid photo of the same field as Figure 3.

Figure 3. Reference spot numbers

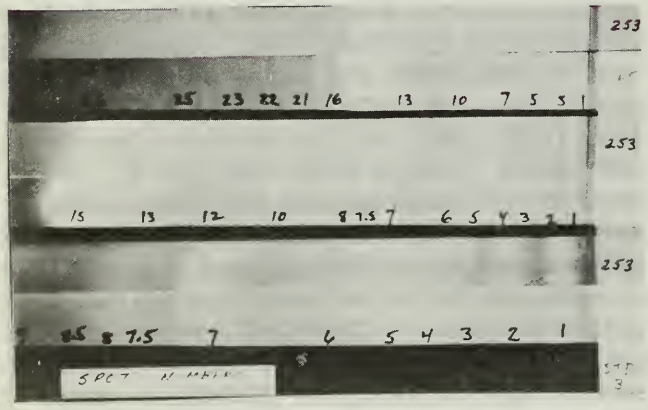


Figure 4. Reference spot numbers, same field as Figure 3

Because of the high cost of color printing, it will usually be necessary to use black and white photos in publications. Figures 3 and 4 illustrate the difference between color and black and white.

Table 1 lists the fluorescent spots by number giving their color, both visible and fluorescent under the two exciting sources, and also their mobility relative to picric acid and HMF. In the Table, the underlined fluorescent colors indicate that the color is more intense under this excitation, and this is an excellent point for differentiating nearby spots.

There are few generalizations that can be made. The lower numbers, which travel the shortest distance in electrophoresis, are generally yellow in visible light, while the higher numbered substances, which move farther are generally brown. The fluorescent colors are generally yellow for the low numbers and blue for the higher numbers with some black (absorbing) spots at the highest numbers.

This tabulation is by no means complete, nor is it meant to be. But it does give a set of reference spot numbers all through the region of sugar colorants that can and will be used in describing the sugar colorants, where they came from, and where they go. As other colorants are found, they will be given fractional numbers in between these. Several fractional numbers are already included.

SEPARATION OF COLORANT FROM SUGARS

The major problem in the use of PE for analyzing sugar colorant is in getting a high enough colorant concentration relative to sugar so that enough material can be put on the paper to see the colorant and yet not be overloaded with sugar, as was previously described.

In making a survey of refinery processes it will be necessary to examine some fairly pure syrups; therefore, a method for separating the colorant from most of the sugar will be needed. We could separate the sugar by boiling off the water under vacuum in a laboratory crystallization but, in the ultimate, we could only reach a mixture analogous to molasses which is about 2/3 sugar. This is still too much sugar for a good electrophoresis analysis, so another method is required.

It is too much to expect that there will ever be found a method that will quantitatively separate all the colorants as a group from all the sugars. We will be satisfied with a procedure that will separate most of the colorants from the sugar. Since the object of the separation is to obtain most of the colorants as a group, the separation will obviously have to be gentle and nonselective. This requirement excludes such processes

Table 1. --Fluorescent Spots

No.	Color			M HMF-PIC
	Fluorescent		Visible	
	365	253		
1	Y	Y	Y	.25
2	Y	Y		.26
3	G	G		.34
4	G	YG	Y	.36
5	G	G	Y	.40
6	Y	Y		.44
7	Golden Y	Golden Y	Y	.50
7.5	Purple			.55
8	YG	Y	Y	.58
8.5	B	B		.59
9	B	B		.60
10	Canary Y	Canary Y	Y	.68
11	Purple	Purple		.69
11.5	Purple			.75
12	Orange Y	Orange Y	Y	.77
13	B	B		.86
14	Purple	Purple		.92
15	Blue	Blue		1.00
15.5	Orange	Orange		1.02
16	Deep B	Deep B	B R	1.07
17	Black	Black	R E	1.07
18	B	B	O G	1.09
19	BG	BG	W I	1.10
20	B	B	N O	1.14
21	B	B	N	1.22
22	B	B		1.34
23	B	B		1.46
24	B	B		1.54
25	B	B		1.60
26		Black		1.94
27		Black		2.16
28		Black		2.24

B = Blue, G = Green, Y = Yellow, Black = Quenching of background fluorescence of paper. Underline means more intense coloration

as ion exchange, dialysis, or fermentation which are notoriously very selective. Solvent precipitation or extraction are about the only practical methods left, and it is evident that the solvent must not be greatly different from water. This suggests immediately that alcohols might be suitable solvents. A quick check revealed that sucrose was too soluble in methanol, while the colorants seemed too little soluble in the propanols. Ethanol seemed to be just about right.

ALCOHOL-WATER PRECIPITATION

A large proportion of the sugar colorants were quite soluble in ethanol. Upon increasing the ethanol fraction of the solvent (ethanol-water mixture) to about 85% ethanol, the sucrose began to precipitate out.

Note that this is the reverse of the alcohol insoluble test that is applied to sugars for determination of "gums". In the alcohol insoluble test the ethanol concentration is raised to 75% and the sugar stays in solution. The precipitate in this case consists of higher polysaccharides and other high molecular weight materials that are collectively labeled "gums" (7).

In the present method the ethanol concentration is raised to above 75% to precipitate the sugar and leave the colorant in solution. The method is as follows:

To a solution containing 1600 g. of sugar in 640 ml. of water (70 Brix) was gradually added 8 liters of absolute ethanol with vigorous stirring. The final alcohol concentration was about 92%. The addition took 5 hours. The sugar precipitate was filtered off and the filtrate was evaporated under reduced pressure to a heavy syrup. Almost all of the alcohol and a large part of the water was removed by this evaporation.

Industrial solutions, such as clarified liquor or liquor off bone char, were treated with alcohol directly, just as they were obtained from the refinery.

This process was repeated as many times as necessary, each time on a smaller scale until a solution highly concentrated in colorant with a minimum of sucrose was obtained. The number of times the process had to be repeated depended upon the purity

of the starting material. Granulated sugar and liquors off char required three passes; clarified liquors and raw sugars-two; molasses and affination syrups-one. It was found impossible to completely free the colorant from all the sugars by this method. More invert than sucrose was left with the colorant. Nevertheless, the invert concentration could be reduced to an extent where it would not greatly interfere with PE. Since the precipitated sugar was yellow, especially in the last pass, it was obvious that some of the colorant goes along with the sucrose precipitated out of the solution and is lost. In addition, since alcohol is known to precipitate high molecular weight gums, it is reasonable to assume that some high molecular weight colorants are also precipitated. Nevertheless, those materials that are precipitated are probably slightly soluble in the ethanol-water mixture and at least a chromatographic amount may remain in solution and thus be detected.

Figure 5 demonstrates the effectiveness of the alcohol-water precipitation method. The top trace was obtained from a molasses while the bottom trace was obtained from the colorant extracted from that molasses by the alcohol-water precipitation method.

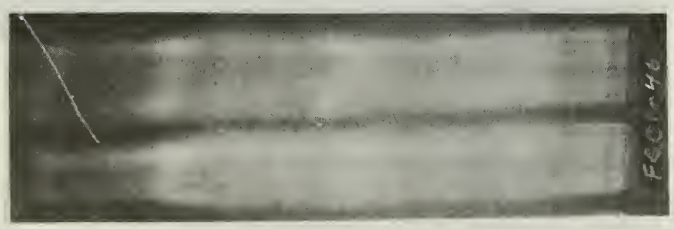


Figure 5. FUPEG of whole molasses (upper trace) and colorant obtained from the same molasses by alcohol-water precipitation of sugar (lower trace). The most prominent bands are (L to R) 15, 10, and 5. The exciting U. V. light was of 365 nm. wavelength. FGC1-46

The molasses FUPEG shows considerable background fluorescence with many bands coming through. The extracted colorant shows less background and more prominent bands, but, most important, all the bands of the original molasses are present in the extracted colorant, indicating that no components discernable by this technique are completely lost. Changes in pH will enhance or suppress some colorant bands. This may be useful in separating individual colorants in a pure state. A detailed discussion, however, is beyond the scope of this report.

Figure 6 is a FUPEG of colorants obtained from raw sugar by this method. Colorants appearing in the region from 1 to 15 are clear and easy to identify. Colorants appearing beyond 15 are somewhat more difficult to identify due to the presence of invert sugar at about this point.

Figure 6. FUPEG of colorants obtained from a Puerto Rican raw by alcohol-water precipitation of the sugar. LF1-111

ETHYL ACETATE-PYRIDINE PRECIPITATION

In an attempt to completely remove the sugars from the colorants, precipitation was carried out in a nonaqueous system. In this case, a sample of raw sugar was dissolved in pyridine instead of water, and ethyl acetate was used as the precipitant in place of ethanol. Figure 7 shows the colorants obtained by

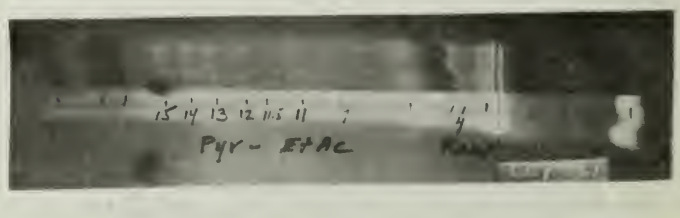


Figure 7. FUPEG of colorants obtained from La. raw sugar by ethyl acetate-pyridine precipitation of the sugar. LF1-101

this method from raw sugar. Again, there are many bands up to No. 15, but few beyond. Neither sucrose nor invert sugar is present. The 253 absorbing band near No. 4 and the three additional bands appearing beyond No. 15 are impurities in the pyridine that could easily be removed by distillation. A fault of this procedure, however, is the limited solubility of the sugar samples in pyridine. Since the number of components found is no greater than with the alcohol-water precipitation method, and since there is a possibility that the completely different chemical nature of the solvent may be introducing more problems than it is solving, this procedure was abandoned as a survey method of separating colorant from sugars.

ETHYL ACETATE EXTRACTION

Another procedure studied was the extraction of colorant from an aqueous sugar solution with ethyl acetate. Standard liquid-liquid extraction procedures were used. The ethyl acetate extract was dried over anhydrous sodium sulfate and then concentrated under reduced pressure.

Figure 8 shows the resulting FUPEG. Invert sugar is completely absent in this case. The colorants present beyond component 15 are clear and easy to identify.

Figure 8. FUPEG of colorants extracted from La. raw sugar solution by ethyl acetate. LF1-115

Difficulty is sometimes encountered during the extraction due to emulsification. If the mixture is allowed to stand, the emulsion will gradually break. This method separates as many colorants as the alcohol-water precipitation method, and usually the same colorants. The advantage is that less invert sugars are included with the colorant. Also it is a quicker and an easier procedure and is the preferred method.

METHYL ETHYL KETONE EXTRACTION

A study was also made of the ability of methyl ethyl ketone to extract colorant. Although the methyl ethyl ketone is partly miscible in water, when saturated with sucrose or NaCl it forms a second phase containing only a very small fraction of water. When a sugar solution of 60 Brix or more was used the addition of NaCl was unnecessary. Figure 9 is a FUPEG showing the colorants obtained by this procedure. Most of the

Figure 9. FUPEG of colorants extracted from La. raw sugar solution by methyl ethyl ketone. LF1-107

colorants appear to be more readily soluble in methyl ethyl ketone than in ethyl acetate. Since both glucose and fructose are slightly soluble in methyl ethyl ketone, a small quantity of invert will also be present in the extract, which makes this method less preferable.

COLORANTS IN PROCESS LIQUORS

It was decided that the ethyl acetate extraction procedure as well as the alcohol-water precipitation method would be used for our survey of sugar colorants throughout the various industrial refinery processes.

Samples were obtained from several different refineries at different times and must be considered as typical rather than specific.

The survey started with cane juice, went through the entire industrial refining process

and ended with granulated sugar. These included samples of raw sugar, clarified liquor, liquor off newly regenerated bone char, and nearly spent bone char, liquor off newly regenerated granular carbon and liquor off nearly spent granular carbon. Finally, the colorants in granulated sugar were studied.

In every case both the alcohol-water precipitation and ethyl acetate extraction methods were used. Sometimes, components not found by one procedure were identified by the other. In cases where two components have the same color and are found adjacent to each other on the paper, a possibility that one could sometimes be mistaken for the other does exist.

Cane Juice

As mentioned earlier, the colorants found in cane juice are: 1, 2, 3, 4, 5, 6, 7, 7. 5, 8, 8. 5, 9, 10, 11, 11. 5, 12, 13, 14, 15, 15. 5, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28.

Raw Sugar

The colorants found by the alcohol-water precipitation method are: 1, 2. 1, 3, 3. 1, 6, 7. 5, 8. 5, 9, 10, 11, 12, 13, 14, 15, 18, 21, 23, 24.

Colorants 2. 1 and 3. 1, have not been previously reported. Their mobilities relative to picric acid and HMF are approximately 0. 29 and 0. 35 respectively. They both fluoresce green under UV light of either 253 nm. or 365 nm.

The components found by ethyl acetate extraction are: 1, 3, 4, 6, 7. 5, 9, 11, 11. 5, 12, 13, 15. 6, 16, 18, 20. 1, 21. Both 15. 6 and 20. 1 are new. Component 15. 6 fluoresces blue at both wavelengths and has a relative mobility of 1. 07. Component 20. 1 absorbs UV light and therefore appears black. It has a relative mobility of approximately 1. 27.

Clarified Liquor

The colorants found by the ethanol-water precipitation procedure are: 1, 2. 1, 3, 3. 1, 6, 7. 5, 8. 5, 9, 11, 13, 14, 15, 18, 21, 23 and 24.

The ethyl acetate extraction procedure yielded the following components: 1, 3, 4, 6, 7. 5, 9, 11, 11. 5, 12, 13, 15, 15. 6, 16, 18, 20. 1, 21, and 23.

Liquor off Newly Regenerated Bone Char

Colorants found by ethanol-water precipitation are: 6, 8. 5, 10, 11, 11. 5, 12, 15, 16, 20, 20. 1, 21, 23, and 25.

Only components 4 and 13 were detected by the ethyl acetate extraction.

Liquor off Nearly Spent Bone Char

As expected, liquor off nearly spent bone char had a greater number of colorants than liquor off newly regenerated bone char. The concentrations also appeared to be greater in the liquor off nearly spent char.

Colorants found by ethanol-water precipitation are: 2. 1, 3, 3. 1, 6, 8. 5, 9, 11, 12, 13, 14, 15, 16, 20, 23 and 25.

Colorants found by ethyl acetate extraction are: 4, 6, 11, 12, 13, 15, 15. 6, 15. 7, 18, 20. 1, 21, and 24. Component 15. 7 has not been previously observed. It has a blue fluorescence at 356 nm. and absorbs light at the 253 nm. wavelength. Its relative mobility is 1. 09.

Liquor off Newly Regenerated Granular Carbon

Components found by ethanol-water precipitation are: 1, 6, 7, 11, and 15. Those found by ethyl acetate extraction are: 1, 10, 12, and 21.

Of all samples studied, including granulated sugar, this particular sample had the least number of color components, which is in agreement with the often observed fact that the purest liquors in the whole refinery are those obtained from a freshly regenerated adsorbent.

Liquor off Nearly Spent Granular Carbon

Colorants found by ethanol-water precipitation are: 4, 6, 7, 10, 12, 15, 18, 20, 20. 1, 21, and 23.

Components found by ethyl acetate extraction are: 11. 5, 12, 13, 15. 6, 17, 18, 20. 1, and 23.

Granulated Sugar

The ethanol-water precipitation procedure indicated the following components: 5, 8. 5, 9, 10, 12, 13, 14, 15, 16, 20, 20. 1, and 28.

Components identified by ethyl acetate extraction are: 5, 8. 5, 12, 13, 14, 15, 16, 20.

Although this study of colorants was by no means quantitative, it was nevertheless obvious that the concentrations of those colorants in granulated sugar were extremely minute. All the colorants obtained from 800 g. of granulated sugar were put on the paper shown in Figure 10. Note that a large amount of colorant remains at the origin. This is typical of granulated sugars

Figure 10. FUPEG (365 nm. excitation only) of all the colorants obtained from 800 g. of granulated sugar by alcohol-water precipitation of the sugar. LF1-103.

and the amount of material remaining at the origin relative to all the colorant increases as the sugar progresses through the various stages of refining. This can be explained in either of two ways. First: this material could originate in the cane and be totally unaffected by any of the purification processes and thus remain unchanged. Its relative amount increases through the various stages of refining only because all the other impurities are being removed. A second, and more likely, explanation is that this is a colorant produced in the course of refining. Since this colorant does not move in electrophoresis, it is undoubtedly of a different chemical nature from sugars or cane pigments. However, it is not the only colorant left in granulated sugar, as seen in Figure 10, where several cane pigments are still very much in evidence.

Summary of Colorants in Process Liquors

A summary of the results obtained from the survey is shown in Table 2. Of the 37 colorants we have found, the following appear in the later stages of refining and these are the most troublesome to the sugar refining industry: 5, 6, 8. 5, 9, 10, 12, 13, 14, 15, 16, 20, 20. 1, and 28. In addition to these, component 11 was found in granulated sugar by the methyl ethyl ketone extraction method, and should also be listed.

Table 3 gives a list of the new colorants found during the course of the survey.

Colorant Precursors

It should be noted in Table 2 that a number of components are removed at some stage of the refining process only to reappear at a later stage. For example, component 14 which is removed by newly regenerated bone char reappears in granulated sugar. This may indicate the presence of a precursor which is not removed by any of the refining processes, but which gradually breaks down into other colorants. Experiments with component 15 indicate this possibility.

A small quantity of component 15 was isolated by water elution from an electrophoretogram of an ethyl acetate extract of raw sugar. Figure 11 shows a FUPEG of component 15 after its isolation. Only No. 15 is present as the faintest trace appearing between the two black spots of the picric acid reference.

The material was then refluxed in water

Table 2. --Sugar Colorants Found in Various Stages of Refining

Fluorescent Spot No.	Cane Juice	Raw Sugar	Clar. Liq.	Bone Char		Gran. Carb.		Gran. Sugar
				Spent	Regen.	Spent	Regen.	
1	XXXXXXX	XXXXXXX	XXXXXXX				XXXXXXX	
2	XXXXXXX							
2.1		XXXXXXX	XXXXXXX	XXXXXXX				
3	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX				
3.1		XXXXXXX	XXXXXXX	XXXXXXX				
4	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX		
5	XXXXXXX							XXXXXXX
6	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	
7	XXXXXXX					XXXXXXX	XXXXXXX	
7.5	XXXXXXX	XXXXXXX	XXXXXXX					
8	XXXXXXX							
8.5	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX			XXXXXXX
9	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX				XXXXXXX
10	XXXXXXX	XXXXXXX			XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX
11	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX			
11.5	XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX	XXXXXXX		
12	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX
13	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX
14	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX				XXXXXXX
15	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX
15.5	XXXXXXX							
15.6		XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX		
15.7				XXXXXXX				
16	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX			XXXXXXX
17	XXXXXXX					XXXXXXX		
18	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX		
19	XXXXXXX							
20	XXXXXXX			XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX
20.1		XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX		XXXXXXX
21	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	
22	XXXXXXX							
23	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX		
24	XXXXXXX	XXXXXXX	XXXXXXX	XXXXXXX				
25	XXXXXXX			XXXXXXX	XXXXXXX			
26	XXXXXXX							
27	XXXXXXX							
28	XXXXXXX							XXXXXXX

Table 3. --Additional Fluorescent Spots

No.	Fluorescent Color		Visible Color	M* HMF-PIC
	365	253		
2.1	green	green		0.29
3.1	green	green		0.35
15.6	blue	blue		1.07
15.7	blue	black		1.09
20.1	----	black		1.27

*The M values reported here are only approximate

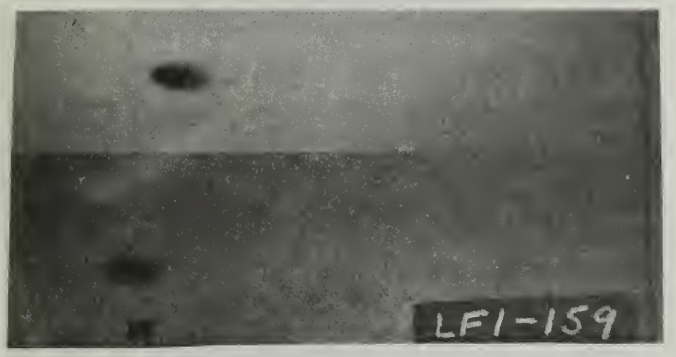


Figure 11. FUPEG of spot 15 isolated by elution from an electrophoretogram. LF1-159

for 2 hours in order to get some idea of its stability. After concentration of the solution it was again chromatographed, Figure 12.

Figure 12. FUPEG of same material as shown in Figure 11 after refluxing in water for 2 hr. LF1-165

Although component 15 was still present, components 3, 21 and 22 were now also present. In addition, some unknown material appeared at the origin. Thus it would appear that 15, a substance that passes through all the known refining processes might be a precursor for a number of other components.

EFFECT OF VARIOUS ADSORBENTS ON SUGAR COLORANTS

A sample of molasses was diluted with water and extracted with ethyl acetate to obtain some sugar colorants. The ethyl acetate extract was dried over sodium sulfate. The ethyl acetate containing the colorant was then reduced in volume and divided into four parts. To the first part was added a few particles of bone char, to the second, Pittsburgh Carbon RB Pulverized, and to the third, Darco S 51. These three samples were allowed to stand overnight and then filtered. Electrophoresis under the usual conditions gave the FUPEG's shown in Figures 13, 14, and 15.

Figure 13. FUPEG of colorant remaining in ethyl acetate after treatment with bone char. LF1-171

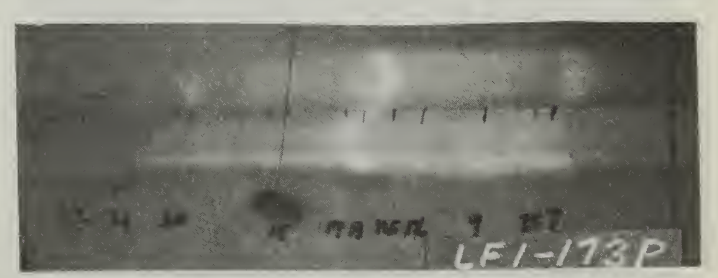


Figure 14. FUPEG of colorant remaining in ethyl acetate after treatment with Pittsburgh Carbon. LF1-173P

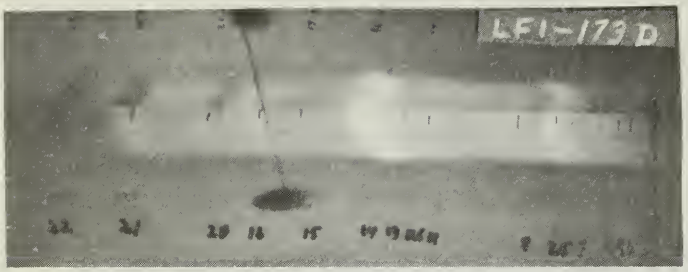


Figure 15. FUPEG of colorant remaining in ethyl acetate after treatment with Darco S 51. LF1-173D

The colorants found were as follows:

Adsorbent	Colorants found
Bone Char	3, 4, 5, 7, 7. 5, 9, 11, 11. 5 13, 14, 15
Pittsburgh Carbon	7, 7. 5, 9, 11, 11. 5, 13, 14, 15, 20, 21, 22
Darco S 51	3, 4, 5, 7, 7. 5, 8, 11, 11. 5, 13, 14, 15, 16, 21, 22, 23

Since bone char appeared to adsorb many of the higher numbered components and the carbons seemed to adsorb the lower numbered colorants, it was decided to try a combination of the two. The fourth sample of ethyl acetate containing the colorants was treated first with bone char for one hour and then, after filtration, with Pittsburgh carbon for thirty minutes. Electrophoresis in the usual manner resulted in the FUPEG shown in Figure 16, in which were found the following components: 11, 11. 5, 13, and 14. Component 13 was by far the most prominent. A faint haze could be seen beyond the marker, indicating the presence of minute quantities of the higher numbered colorants.

It should be stressed that these experiments were all performed in an ethyl acetate medium and at best were only qualitative. They do, however, indicate a specifity of carbon adsorbents of different origin and manufacture for different colorants.

Figure 16. FUPEG of colorant remaining in ethyl acetate after treatment with both bone char and Pittsburgh Carbon. LF1-175

A YELLOW COLORANT

Invariably, as the sugar proceeds through a refinery, the color changes from brown to yellow before becoming white. Yellow colorants are, therefore, of prime interest. Of all the spots that appear in late stages of refining, No. 10 is one of the yellowest when viewed under ordinary white light. It is one of the prominent spots in cane juice so evidently originates in the sugarcane plant. Preliminary work in its separation and identification was described in the 1966 Technical Session (8), where it was called C_2. The material was separated from much of the sugar by first precipitating the sucrose with ethanol. This was followed by water elution from a DEAE cellulose column. Only 5 mg. of material were obtained, but from this amount the following properties were obtained:

1. It contained a carbohydrate
2. It did not contain nitrogen
3. It was of higher molecular weight than sucrose
4. It was soluble in water, and 95% ethanol
5. The visual color was pH sensitive being colorless below pH 5. 2 and canary yellow above pH 7. 5

Other workers (9, 10, 3, 11) had suggested

that yellow components of this nature were plant pigments. The properties mentioned above do not exclude the flavonoid class of plant pigments. Studies were, therefore, undertaken to further identify the colorant No. 10 as a plant pigment.

Filter paper spotted with an aqueous-alcohol solution of No. 10 gave the following color reactions:

1. Under visible light it was pale yellow and under 365 nm. UV light a yellow to yellow brown depending upon pH.
2. When exposed to NH_3 vapor it was yellow in visible light and bright yellow under 365 nm. UV.
3. $AlCl_3$ gave a yellow color in visible light and a bright yellow color under 365 nm. UV.
4. Na_2CO_3 gave a yellow color.

In concentrated sulfuric acid, it formed a yellow-orange solution that fluoresced brightly under 365 nm. UV.

In aqueous sodium hydroxide it gave a yellow solution that had no tendency to turn brown.

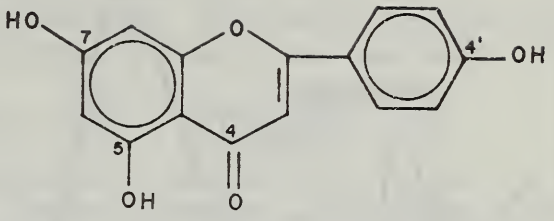
Comparing these properties to the standard color reactions of plant pigments (12) identifies spot No. 10 as a flavone.

The effect of various substituent groups in flavones upon their ultra-violet absorption spectra has been extensively documented. The reader is referred to (12) for details which fill an entire book.

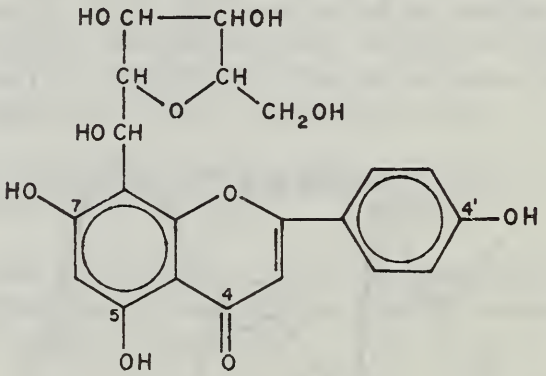
ABSORPTION CURVES OF NO. 10

A sample of No. 10 was further purified by paper chromatography using butanol-acetic acid-water developing solvent. The eluted sample gave only one spot by P. E. The absorption spectra in ethanol, sodium ethylate, sodium acetate, and $AlCl_3$ are given in Figures 17, 18, and 19 and compared with

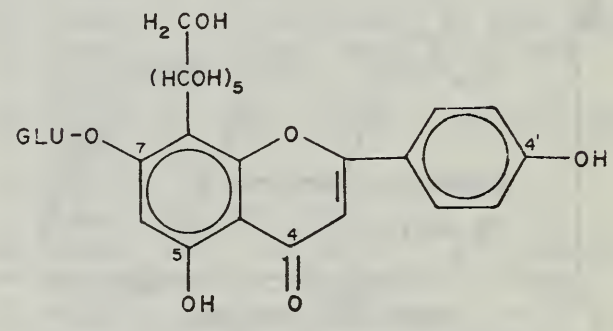
apigenin ----



and two of its derivatives, vitexin



and saponarin.



It is seen that the general shape of the absorption curves of ethanol solutions are similar to those of apigenin and its derivatives. The shift in absorption peaks in sodium ethylate solution (Fig. 17) is also in keeping with this class of flavones. The lack of an increase in optical density at the higher wavelength in this solvent is interpreted to mean that a free hydroxyl does not exist in the 4' position.

In sodium acetate solution (Fig. 18) the absorption peaks and optical densities are quite similar to apigenin and saponarin.

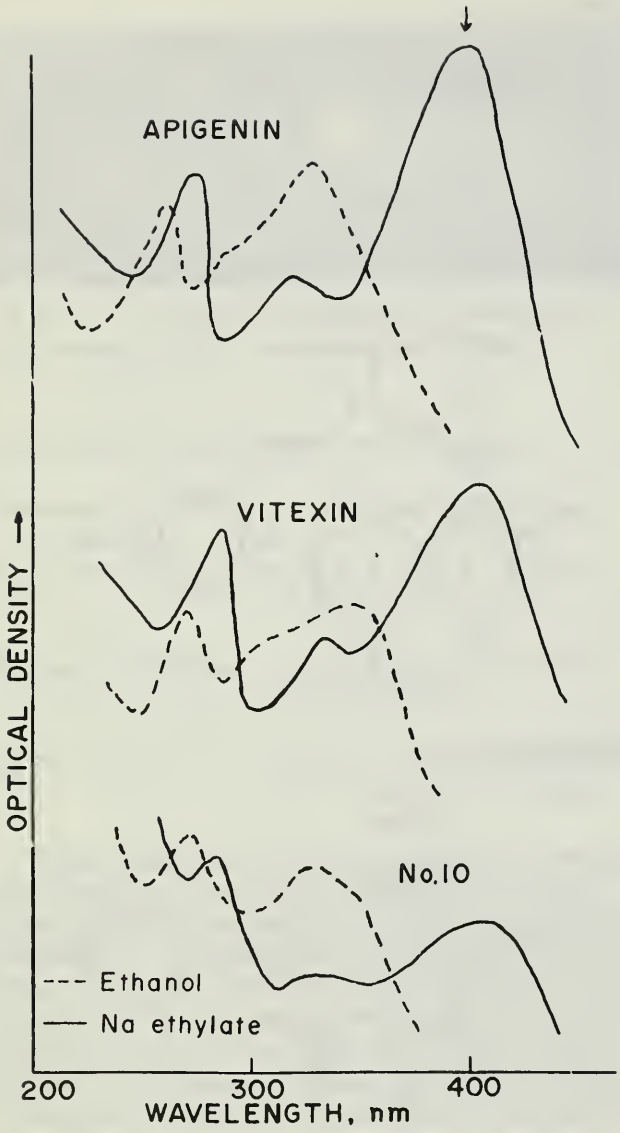


Figure 17

The enhancement of the peaks at 270 nm. is interpreted as a free phenolic group at the 7 position. In the presence of $AlCl_3$ (Fig. 19) one observes the four peaks characteristic of apigenin derivatives caused by the four equilibrium forms of the meta complex with the free hydroxyl at position 5 and the oxygen at position 4.

High voltage electrophoresis of apigenin, vitexin, saponaratin* (the aglucoside of saponarin)

*Vitexin and saponaratin samples kindly furnished by Dr. M. K. Saikal, Forest Products Laboratory, Madison, Wisconsin

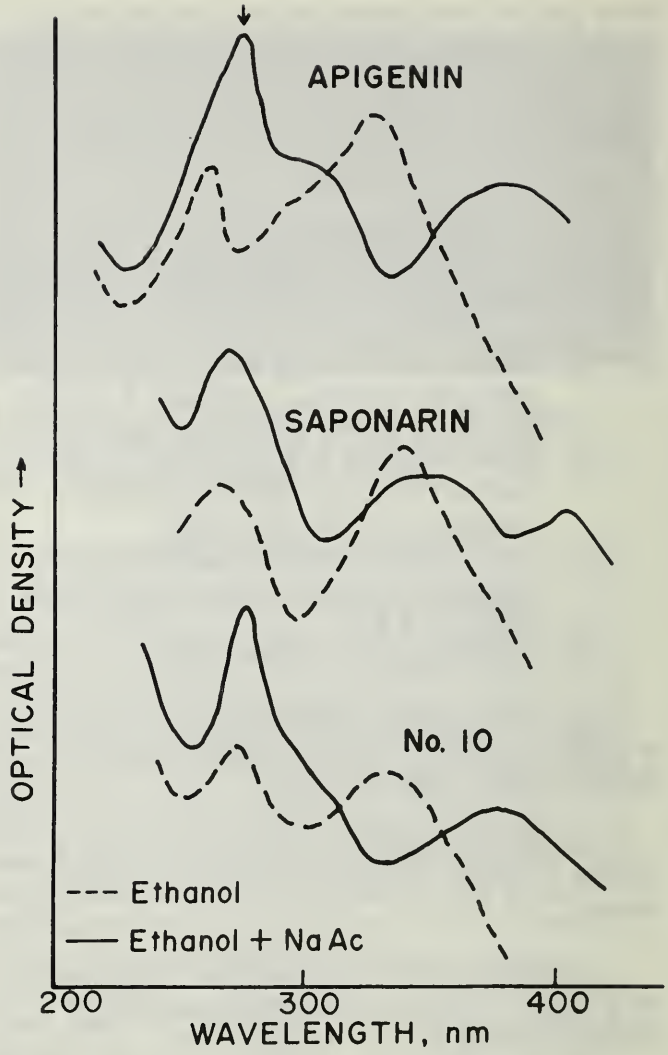
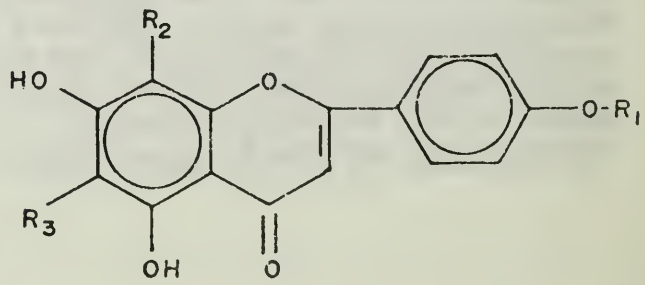


Figure 18

and No. 10 in 0. 05M sodium borate solution gave four different mobilities which indicates that all four substances are different.

In summary all of our data indicate that No. 10 is a flavone of the apigenin class, with the following general formula.



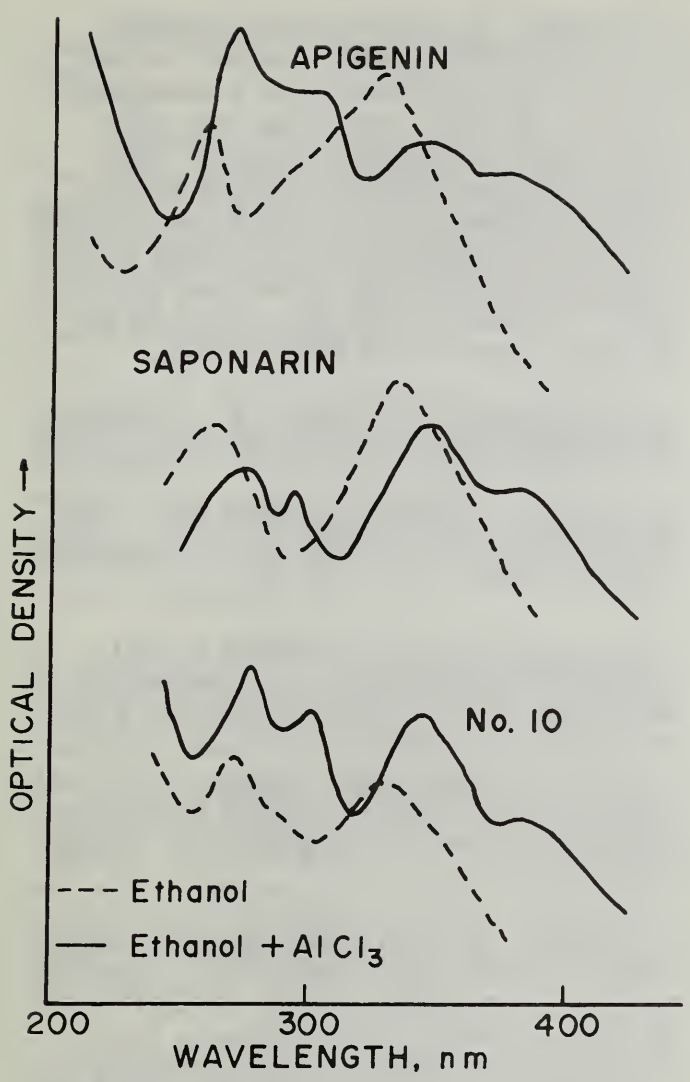


Figure 19

The most probable points of carbohydrate substitution in No. 10 are at the R_1, R_2, or R_3 positions. The exact structure remains to be determined.

The color, basic structure, and primary chemical reactions are independent of the R's. It may be that some of the other sugar colorants are of the same or similar basic structure with different R's.

NO. 10 AS A COLORANT IN TYPICAL SUGARS

The attenuation index of a solution of No. 10 was measured at pH 7. The concentration of colorant was 1.07 mg. in 3 ml. and the transmission at 420 nm. in a 1 cm. cell was 90%. The specific absorption index per gram of colorant was calculated to be:

$$a_{10} = \frac{-\log T}{bc} = \frac{(-\log 0.90)(3)}{(1)(0.00107)} = 150$$

This may be compared with the color of sugar liquors measured under similar conditions. Liquors off char are typically of a yellow color of about a* = 0.1 per gram of sugar. If all the colorant is material of a specific absorption index similar to that of No. 10, then the total amount of material causing the color would be given by:

$$\frac{0.1 \text{ color/g. sugar}}{150 \text{ color/g. colorant}} = \frac{0.0007 \text{ g. colorant}}{\text{g. sugar}} = .07\%$$

These calculations are presented only as an indication of the probable order of magnitude of weight of impurity.

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DISCUSSION

T.M. Rinehart (Atlas): In the liquors that were decolorized with different adsorbents,

how much color was taken out compared to the usual refinery operation?

L. Farber (S. R. R. L.): We don't have a quantitative study at this time. This is purely qualitative. We can't say how much has been taken out.

T. M. Rinehart: No color measurements were made at all?

L. Farber: We plan to do this, but we haven't yet.

T. M. Rinehart: Can you tell me what dosage was used for the various carbons and chars?

L. Farber: Just a few particles of either carbon or char were used. This was purely qualitative.

W. L. Reed (Revere): You showed pictures using several different wavelengths on the same slide. How did you do that?

L. Farber: They were double exposures. We first put the paper electrophoretogram in our chromatoview box. In order to get the double exposure, we covered one half with a piece of tin sheet painted black and took the shot using one source. We then moved this black tin sheet over to the opposite side and changed sources and took the shot again on the same film.

W. L. Reed: Did you use regular commercial Ektachrome X film that anyone can buy?

L. Farber: Yes, and an ordinary old-fashioned 35 mm. single lens reflex camera.

J. F. Dowling (Refined Syrups): About the spot that develops on the origin, which is essentially breakdown products: when you treated your raw liquor in the lab with bone char and activated carbon, I noticed that the spot at the origin didn't develop as strongly as it did with granulated sugar. Do you find this to be generally true?

L. Farber: We did not completely simulate refinery conditions. We were not working with liquor, but with colorants extracted from molasses with ethyl acetate. It was done at room temperature, in a nonaqueous system. We have, since that time, also made a study in aqueous solutions. We simply evaporated down our ethyl acetate extract and took it back up with water. There again we saw differences in the adsorptive powers of the different carbons and bone char, but they were not as spectacular as the ones I showed with ethyl acetate.

J. F. Dowling: Can you give us an estimate of the molecular weight of these compounds?

L. Farber: No, we don't really know what they are yet. That is what we are just starting to do now.

E. J. Culp (American): Looking at your beautiful colored slides, I get a subjective feeling that some of these stripes are placed at more or less uniform intervals. At least one gets that impression looking at them this way. Have you noticed anything like this? And if so, do you put any particular significance in it?

L. Farber: No, I think this is just a coincidence. It just happened that way. Some of them are very close together. In fact we find some of them almost sitting on top of each other. We could see the tail of one sticking out on one side and the head of the other sticking out on the other side.

K. Schoenrock (Amalgamated): This happens to be an area where we have more questions than answers, and I have several questions, but first of all I would like to know if you have compared notes with the work that is going on at the University of Vienna under Professor Prey, who is also doing extensive work on isolation and identification of the colorants.

L. Farber: No, we have not communicated with Dr. Prey but does he work with cane sugar?

K. Schoenrock: I think they worked primarily with beet sugar products, but I

imagine there are some similarities.

Apparently there are only three or four of these colorants that carry through to the sugar, and these are the dangerous ones that we should concentrate our efforts on. It looks like they go through carbon treatment and so on. I wonder what ion exchange does to these colorants?

L. Farber: We've made a few preliminary tests with ion exchange, and there appear to be differences there also in the ability to adsorb. But we haven't studied this in much detail. We have examined waste regenerants from ion exchange and found them to be very rich in component 10.

K. Schoenrock: Would the concentration of the colorant that carried through change, increase or decrease through the process?

L. Farber: Again, at this point we can give you very little information on the quantitative aspects. We have been, up to now, primarily concerned with seeing just which colorants are the most important to study. Now we're going to see how much of them are present and what they are.

N. H. Smith (C&H): Is it possible that there was some overlap in colorants, so that a color might be a combination of, for instance, blue and yellow, giving a green streak which might disappear as you ran the electrophoresis longer?

L. Farber: There is the possibility that one band is sitting on top of another, and so we can miss it, but I haven't seen anything of this with certainty. Some come out very, very close. I know that 7 and 7.5 are very, very near each other. But we could see them separately, since one of them tends to fluoresce more in one wavelength and the other in another wavelength.

N. H. Smith: We have a lack, in the literature: the name for these papers after we run them. Some refer to a chromatographic paper and this isn't quite a suitable term. I think we need a name for the results of the electrophoresis.

L. Farber: We have discussed this on several occasions. Perhaps electrophoretograms. Joe Bemis says electrofluorescograms. But since it is going to get abbreviated all the way down to 2 or 3 letters eventually anyway, perhaps we should call the process PE for Paper Electrophoresis which is, after all, the most essential part of the name. The high voltage part of it is only a convenience, not a fundamental difference. The results of the process which are usually indicated by the suffix -gram would then become PEG. When we view them under ultraviolet light we see the Fluorescence from the Ultra-violet excitation of our PEG's, or FUPEG, which we can either look at or photograph.

N. H. Smith: (added in correspondence): I recently found the word "pherogram" used in a current publication. This is sufficiently short for acceptable use.

K. Schoenrock: I had one other question relative to the absorption bands of these colorants that carry through to sugar. Now these are apparently the ones that give trouble with color in sugar. Do you have any information on their absorption in the visible and UV?

L. Farber: No we haven't studied this yet.

K. Schoenrock: It would seem to be better to measure color at an absorption peak rather than at arbitrarily selected wavelengths such as 420, 560, or 455 nm.

F. G. Carpenter (S. R. R. L.): At this point we are working on the isolation of one component. When we get a sufficient amount of it electrophoretically pure, then we'll measure the absorption throughout the visible and ultraviolet. As long as we still have a mixture, we are no better than we were with raw sugar. What's the use of just getting it only partly purified? Let's get it separated completely and then we'll see what the absorption is for a single component.

S. E. Bichsel (Holly): I wonder if you'd care to comment on some of your thinking concerning the mechanism of the interference of invert? Are we complexing there? Do you have any ideas on this?

L. Farber: Nobody knows for sure, I believe. The invert is there in a large mass and becomes the largest component in the entire system, and tends to block the remaining smaller quantities from getting past it. The fluid tends to flow around the invert and forms a narrower band on the other end. This is what we think may be the reason. Perhaps it is in sufficient quantity to overcome the buffer and upset the pH, conductivity, ionic strength, etc., of the buffer. This would produce an uneven voltage gradient and hence an uneven advance. We're not sure of that either.

S. E. Bichsel: Also we noticed that your entire study was done with borate buffer at a little over pH 9. Did you experiment with any other buffer systems and, if you stayed with the borate system, did you try to make any pH changes and determine whether these materials that migrate-I suppose toward the positive pole-are in fact amphoteric and can, at different pH's, migrate towards the negative pole?

L. Farber: This may be a possibility. Long before I arrived on the scene, Dr. Gross, Dr. Carpenter, and many others found that the borate buffer seemed to give the best possible results. A number of other systems were tried (1). Sodium borate buffer was found to be the optimal one, and that's the one we are using. I have not myself gone into experimentation with other types of electrolytes.

S. E. Bichsel: I noticed that you are using a rather high voltage of 100 volts per cm. Evidently this apparatus that you used definitely had a water-cooled block; was it refrigeration cooled too?

F. G. Carpenter: The apparatus is essentially that described by Gross (2). It is water-cooled and we have a refrigerator. We keep the temperature at about 14 or 15° C.

As you say, the problem is the heat load. We put several kilowatts into a piece of paper and keeping that cool takes some heat transfer. The essential feature is pneumatic pressure squeezing the paper between the water cooled plates. Thin polyethylene is used for electrical insulation.

K. J. Parker (Tate and Lyle): Dr. Farber, is it true that only components which give fluorescence are in fact colored, and do all colored substances give a fluorescent spectrum on your separation?

L. Farber: All the compounds that we can see visibly as colored seem to give fluorescence. In addition to that, we see a number that give fluorescence that are not colored as such. But now that I'm beginning to get greater and greater concentrations of these, for example, No. 15, which we originally listed as not colored, there seems to be a faint yellow hue to it--I'm not sure whether this is due to a contamination, or if it's really 15 which is giving the color.

K. J. Parker: It's certain that one could learn quite a lot about the nature of these substances from their fluorescence spectra. You've got a good separation and the fact that you've got greens and blues suggest that they have characteristic fluorescence spectra. Have you attempted to record these fluorescence spectra and from this possibly get some information on the type of compound which is involved?

L. Farber: We feel this is still a bit premature. We would like to get these compounds separated in a pure state, first, then we will study them.

METHODS FOR SEPARATING SUGAR COLORANTS

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INTRODUCTION

Relatively new methods for the isolation and characterization of sugar colorants have spurred interest and added impetus to the study of colorants and refinability in several laboratories. These methods include gel filtration for the separation and fractionation of colorants, and high voltage electrophoresis for their characterization.

There is a variety of approaches to the problem of colorant identification among the various laboratories; each study can contribute knowledge that is unique. However, one consequence is a diversity of conclusions concerning the qualitative and quantitative significance of particular colorants.

This report is concerned with a comparison of some of the methods which can be used to obtain colorants, rather than a detailed study of particular colorant types. The data, when related to the results of other investigators, may contribute to a clearer picture of the role of the various kinds of colorants in refinability problems.

Separation Methods

The colorants to be compared were generally obtained by known methods. Essential to the various methods is the separation of colorant from the bulk of the colorless substances present, especially sugars, which generally constitute the major diluent.

The separation methods used are based on 1) differences in molecular size (dialysis, gel filtration), 2) precipitation (basic lead acetate, methanol), and 3) adsorption (bone char, ionic and non-ionic resins, gel filtration media). The starting material for each of the separations reported here was Hawaiian factory molasses.

Characterization Methods

The colorant samples obtained by the above methods were characterized by spectral measurements. Spectral features of importance in comparing isolated colorants with each other, as well as with the original colored material, include general shape of the spectral curve (presence of peaks), variation with changes of pH, and absorptivity (absorbance per unit of concentration).

The samples were also subjected to high voltage electrophoresis, the value of which has been demonstrated by Gross (1) and by McDonald and Carpenter (2). Although this technique adds little to our knowledge of the quantities of colorants in the original sample, it can provide an excellent means of qualitatively estimating a number of colored or colorless substances which may be present.

In addition to characterizations of the isolated colorant fractions, spectral and electrophoretic determinations were made using the original molasses. For comparison, the same characterization methods were applied to a sample of freeze-dried raw cane juice (Variety CP52-68P, supplied by Dr. F. Carpenter), and to a hot water extract of air dried cane leaves (supplied by Dr. C. C. Tu, HSPA).

EXPERIMENTAL SECTION

Separation of Colorants

Dialysis

Dialysis, used by Binkley (3) to isolate the browning polymer from final molasses, is a satisfactory method for providing high molecular weight colorant free of sugar and ash, minimizing conditions which might cause chemical changes during the separation.

It is a highly selective method, wherein low molecular weight colorants are discarded along with the sugar.

A sample of non-dialyzable molasses colorant was prepared by placing cellophane dialysis tubing, with the ends tied off and containing factory molasses, in beakers of distilled water. The water in the beakers was changed daily. When the loss of color through the membrane had appeared to diminish to a very slow rate, the contents of the cellophane bags were concentrated under vacuum to a small volume, filtered through a millipore filter (0.45μ pore size) to remove insoluble matter, and the darkly colored solution was further dialyzed. This time the distilled water in the beaker was continuously displaced with fresh water. The solution was finally concentrated under vacuum, filtered again, and taken to dryness in vacuum.

Gel Filtration

Separations by dialysis are based on molecular size considerations. An alternative method giving a variety of fractions is that of gel filtration. By passing diluted molasses through a column containing a gel such as Sephadex G-10, fairly discrete fractions can be obtained. The volume of solvent required to elute each fraction depends partly on the molecular size of the solute (large molecules are displaced from the gel more readily than small ones), and partly on the extent of adsorption of solute by the gel. In the fractionation of molasses, although a significant amount of colorant was eluted with the fraction containing the sugars, other fractions free of sugar were obtained. (A more detailed description of the applications of gel filtration techniques was presented at our 1966 Technical Session (4). These fractions were concentrated to a small volume by vacuum evaporation, and finally taken to dryness by evaporation on watch glasses with mild heating. The contents of each watch glass, generally a few milligrams of solids, could be scraped off the glass and stored until needed.

Precipitation of Colorants with Basic Lead Acetate

Methods for separating colorants from sugar by precipitation can also be used. Basic lead acetate is extensively used for clarifying samples in preparation for quantitative polarimetry. After nearly quantitative precipitation of colorants from molasses with this reagent, the separation of colorants from the lead salts can be effected either by precipitation of lead sulfide using hydrogen sulfide or by precipitation of lead carbonate using ammonium carbonate. The latter method was employed in our tests.

Molasses was diluted with water and mixed with a quantity of basic lead acetate solution in excess of the amount producing precipitation. The solids were isolated by centrifugation, washed by resuspending in water and again isolated by centrifugation. The solids were then suspended in ammonium carbonate solution and mixed well. Centrifugation produced a very dark solution and an almost colorless precipitate of lead carbonate. The solution was concentrated to a small volume by heating under vacuum. Removal of the excess ammonium carbonate was indicated by copious gas evolution, which ceased before the concentration step was completed.

Precipitation of Alcohol Insoluble Colorants

Another procedure for the isolation of colorants by precipitation is based on the limited solubility of some colorants in methanol. When this procedure is applied to solutions of raw sugar, about one third of the color is removed from the sugar. The extent of precipitation is pH-dependent; increasing quantities of darkly colored precipitates are obtained as the alkalinity is increased.

About 200 g. of molasses was mixed with about 600 ml. of methanol and sufficient concentrated ammonium hydroxide to give a pH reading of 8.9. The solids, separated by filtration, were suspended in water and the water insolubles were removed by centrifuga-

tion. After adjustment to pH 3.0 with hydrochloric acid, the now darkly colored solution was diluted with methanol. An alcohol insoluble fraction which precipitated was separated by centrifugation. To the aqueous methanol solution, which gave a pH reading of 4.4, was added ammonium hydroxide to pH 5.4. Additional solids precipitated and were again separated by centrifugation. This process was repeated three more times, providing additional solids insoluble in aqueous methanol above pH 6.4, 7.5, and 8.7, respectively.

Isolation of Adsorbed Colorants

Several procedures for isolating colorants involve an initial adsorption of colorant by an adsorbent, followed by elution of colorant with an appropriate solvent. Perhaps the most obvious application of this principle is the extraction of colorants from spent bone char. In studying sugar colorants Zaorska (5) used aqueous pyridine to extract colorants from spent active carbon. Other solvents examined here in addition to pyridine include isopropyl alcohol, acetic acid, and ammoniacal methanol.

A sample of fines (through 65 mesh) from our best grade of regenerated service char was slurried with diluted molasses for about 15 minutes. The char was then washed free of sugar. A portion of the washed char was mixed with aqueous pyridine (44% by volume). The filtered pyridine extract was concentrated in vacuum with gentle heating to dryness. The residue was redissolved in distilled water, filtered, and concentrated in vacuum to a small volume. Additional portions of the water-washed spent char were given treatments similar to the above, using acetic acid and isopropyl alcohol. Following the isopropyl alcohol treatment, which had yielded very little color, the same char was extracted with 1% ammoniacal methanol to produce a fourth char extract.

Samples of colorants which had been adsorbed by ion exchange resins were also obtained. Molasses was slurried with the resin which was then thoroughly washed with distilled water to free the resin of non-adsorbed or weakly adsorbed matter. The resin, packed into a column, was then eluted with a suitable solvent. The extracts were then concentrated in vacuum to small volumes and finally dried on watch glasses. In this manner an anion resin, IRA-401-S, in the chloride form, was extracted with methanol. Subsequent extraction of the same resin with 1N ammonium hydroxide produced additional colorant solution. A cation resin, IRC-120, in the acid form, yielded no colorant by methanol extraction. However, extraction with 1N ammonium hydroxide did liberate colorant.

Colorant samples were prepared using a non-ionic resin, Amberlite XAD-2, as the adsorbant. Colored extracts were obtained using methanol or dilute ammonia as the solvent.

In working with the gel, Sephadex G-10, it was found that elution with an acidic solvent removed some colorants extremely slowly. An acidic slurry of Sephadex was prepared, and the Sephadex was exhaustively eluted with water. After the Sephadex had been extracted with sufficient water to remove all of the sugar, a large volume of tailings was collected. This was concentrated and taken to dryness to produce one sample of colorant. Subsequent elution of the Sephadex with a relatively small volume of 0.015N ammonia desorbed an additional amount of colorant which was similarly concentrated and dried.

Spectral Measurements

An aqueous solution of each colorant was prepared at known concentration by diluting a known weight of solid sample (or liquid sample of known RDS) to volume in a 5 to 25 ml. volumetric flask. Aliquots of the solution were transferred to three volumetric flasks and diluted to volume with buffer of pH 4, 7, and 9. The buffers were prepared by mixing 1N ammonia with 1N acetic acid to the appropriate pH.

Spectra were determined using a Bausch and Lomb 505 Spectrophotometer in the range of 240 to 540 nm. The absorptivity values were calculated by dividing the absorbance (at 420 or 275 nm.) in a 1 cm. cell by the concentration of sample in g./ml.

Electrophoresis

The apparatus used for electrophoresis was built at C. and H. The power supply can provide up to 10,000 volts of unfiltered direct current at a load of up to 500 ma. of current. To provide cooling, the electrophoresis paper is immersed in a Lucite tank containing Varsol, a high boiling cut of kerosene. The Varsol is pumped out of the top of the tank, circulated through an ice water bath and back into the bottom of the tank. Using this system, electrophoretic separations were made at 5000 volts and about 200 ma., maintaining a temperature in the tank not exceeding 15° C. The paper support for electrophoresis was Whatman 3MM, 5" wide and 22" long. Buffer compartments at the top and bottom of the tank were equipped with platinum electrodes. The spacing of the buffer compartments provided a potential of about 100 volts/cm.

Sodium borate buffer was prepared by adding sodium hydroxide pellets to 0.2 M. boric acid to give a pH of 9.0 to 9.2. Buffer of this strength (equivalent to 0.05 M. sodium tetraborate) provided sufficient conductance to permit migration of colorant without overtaxing the capacity of the cooling system.

The paper was prepared by wetting with buffer solution and blotting the paper to remove excess buffer. Concentrated solutions of colorant samples were transferred to a line 4" from the cathode end of the paper by spotting with a platinum loop of wire. Several spots could be run simultaneously by spotting at 1/2" intervals. Application of high voltage for 20 minutes was sufficient to obtain satisfactory separations. The completed pherograms were air-dried to remove water and Varsol.

It was found that intense yellow spots generally faded to near invisibility as the paper dried. However, these visibly yellow areas coincided with yellow or blue fluorescent areas seen when the dried paper was viewed under ultra-violet light. Thus, viewing by ultra-violet light was the preferred method for comparing the dried pherograms.

RESULTS AND DISCUSSION

Spectral Measurements

Four parameters were selected to compare spectral data on isolated colorant fractions. These are the absorptivity, the absorptivity ratio, the indicator value, and the wavelength of maximum sensitivity of color to pH changes.

The absorptivity is dependent partly on theoretical considerations, such as the size of the colorant molecule and on the (wavelength dependent) probability of an electronic transition involved in light absorption. Since we are working with mixtures, the absorptivity is also dependent on the ratio of colorant to total solids in the mixture. These various causes for absorptivity variations cannot be separated if the colorant concentrations are unknown. However, as a gross approximation, we can use the absorptivity as an index of colorant purity for measurements made at a given wavelength, when comparing mixtures of similar composition. For this study the absorptivity at 420 nm. was chosen since this wavelength is in the visible region of the spectrum and is the generally accepted standard wavelength for sugar color measurements.

The spectral data are presented in two parts. In Table 1, potential starting materials for the isolation of colorants are listed. This report is limited to the results obtained with molasses, although some separation methods can be applied to cane leaf extracts, raw juices or raw sugar. Apigenin* was included for comparison because of the Cane

*Available as Cat. No. 12, 355-2 from Aldrich Chem. Co.

Table 1. --Optical Properties of Colorant Sources

Colorant Source	Absorptivity, pH 7		I. V. $\frac{a_{pH\ 9}}{a_{pH\ 4}}$ 420	λ of Max. $a_{(9-4)}$
	420 nm.	a_{275}/a_{420}		
Washed Raw Sug.	0.6	11	3.8	380
Molasses	180	9	2.3	380
Raw Juice	17	14	2.7	385
Leaf Extract	180	14	10	380
Apigenin	3930	8	52	390

Sugar Refining Research Project work (2) showing that one of the colorants we may encounter has been identified as a substituted flavone of the apigenin series.

Comparison of the absorptivities of the colorant sources listed indicates that the colorant content of molasses is about 300 times that of an affined raw sugar, and about 10 times that of raw cane juice. It is somewhat surprising that a hot water extract of cane leaves is as intensely colored, on a solids basis, as is molasses. The absorptivity of apigenin is 30 times that of molasses or the leaf extract. If all the colorants were of the apigenin type, we could estimate the colorant content of molasses or leaf extract to be about 3%, since apigenin represents 100% colorant.

Raw juice is about 30 times as colored as is a washed raw sugar. Thus, although during factory processing there is undoubtedly development of color through sugar degradation mechanisms, degradation isn't necessary to explain the amount of colored substances in raw sugar.

The value for the absorptivity of molasses, 180, can be compared with the absorptivity values obtained for colorant samples isolated from molasses by various techniques, as shown in Table 2. These values range from a low of 47 for the second gel filtration fraction to a high of 2980 for an ammonia eluate of a non-ionic resin column. The low value of 47 is expected, since this fraction also contains the bulk of the sugars of the original molasses sample. The third gel filtration fraction, which also has a low value (190), contains the bulk of the ash constituents of the original sample. Other colorants which have low absorptivity values are the isopropyl alcohol extract of spent char (200), and the colorant displaced from an anion resin with dilute ammonia (190). Isopropyl alcohol was not a good solvent for extracting colorants from char, but was included in the table because the colorant that was extracted showed a relatively high sensitivity of color to changes in pH. The ammonia extract of the anion resin was also not greatly colored. Its inclusion in the table illustrates an insensitivity of color to pH changes.

Except for a few exceptions discussed, the various samples appear to be significantly richer in colorant than the molasses from which they were prepared. A few samples have absorbances approaching that of a pure colorant, apigenin. We should not place this value (3930) as an upper limit, however, since the absorptivity can be expected to vary widely among pure colorants, depending on the spectral characteristics of the individual substances.

The second parameter listed in the table, the ratio of absorptivity at 275 nm. to that at 420 nm., was used as a measure of variation of composition among the samples. Many of the colorant mixtures we are discussing have prominent absorption maxima near 275 nm., which is well within the ultraviolet region of the spectrum. This absorption peak, which

Table 2. --Optical Properties of Colorant Fractions Isolated from Molasses

Method of Isolation	Absorptivity, pH 7		I. V. $_{420}$ $a_{pH\ 9}/a_{pH\ 4}$	λ of Max. $a_{(9-4)}$
	420 nm.	a_{275}/a_{420}		
Dialysis	680	4	1.5	380
Gel Filtration:				
Sephadex G-10 Fraction 1	1310	4	1.4	-
2	47	13	1.4	-
3	190	12	1.6	365
4	1640	9	2.7	375
5	1235	11	2.5	395
Lead Acetate Precipitate	565	7	1.9	375
Alcohol Insolubles: pH 4.4	425	6	1.8	380
5.4	705	7	2.0	385
6.4	515	8	2.3	385
7.5	445	8	2.5	390
8.7	660	8	5.5	385
Char Extracts:				
Aqueous Pyridine	1200	8	2.5	385
Acetic Acid	455	9	2.3	375
Isopropyl Alcohol	200	5	6.9	360
Methanol - Ammonia	690	11	3.3	370
Resins:				
IRA-401-S-Methanol	1680	9	2.7	380
IRA-401-S-Ammonia	190	7	0.9	-
IRC-120-Ammonia	495	12	1.9	360
XAD-2-Methanol	1230	10	3.3	385
XAD-2-Ammonia	2980	5	2.5	390
Acidic Sephadex:				
Acid Tailings	1300	10	10	380
Ammonia Extract	2340	8	2	385

can be seen in the spectrum of molasses (Figure 1) can be caused by colored or colorless components of the mixtures. One advantage of such a ratio is its independence from the concentration considerations involved with our first parameter, the absorptivity. Further, a low ratio is characteristic of colorants with relatively flat spectra in the visible region. Such colorants typically appear darker to the eye than expected on the basis of their 420 nm. absorptivities.

The absorptivity ratio for colorant sources ranges from 9 for molasses to 14 for leaf extract and raw juice. Since colorless organic compounds such as hydroxymethyl furfural may contribute to the short wavelength absorptivity and thus increase the ratio, we might expect that isolated colorants would

have a relatively low ratio if the method used for isolation excluded low molecular weight substances. In fact, we find that non-dialyzable colorant and the first eluant of gel filtration have low ratios. Both methods are selective for high molecular weight compounds.

The absorptivity ratio for apigenin is comparable to that for molasses. The high ratios found for several isolated colorant samples, including some gel filtration and extracted resin samples suggests that these methods may be selective for particular colorless but ultraviolet absorbing substances.

Another ratio, the absorptivity at pH 9 divided by that at pH 4 (determined at 420 nm.), is also concentration independent. This parameter has been defined as the indicator value (I. V.)(6). The I. V. is also a measure of colorant composition variations. While the (a_{275}/a_{420}) ratio can be affected by the presence of colorless components, the I. V. generally cannot. The I. V. may be considered an approximate measure of the proportion of the colorants in a mixture which are sensitive to changes in pH. (However, I. V. cannot distinguish between high proportions of slightly pH-sensitive colorants and low proportions of highly pH-sensitive colorants.)

The wide variation in I. V. has previously been related to variations in refinability of raw sugars (6), with easily decolorized raws exhibiting a relatively high I. V. The I. V. for Hawaiian washed raws generally varies between 3 and 8. The I. V. for both a Louisiana raw juice and Hawaiian factory molasses is lower, while that of a hot water extract of dried cane leaves is higher. The I. V. for apigenin is very high. Although colored degradation products of sugars can be prepared which show some sensitivity to pH changes, we have been unable to prepare, under laboratory conditions simulating factory processing or refining, colorants showing high sensitivity. We may expect therefore, that colorant samples showing a high I. V. represents fractions enriched

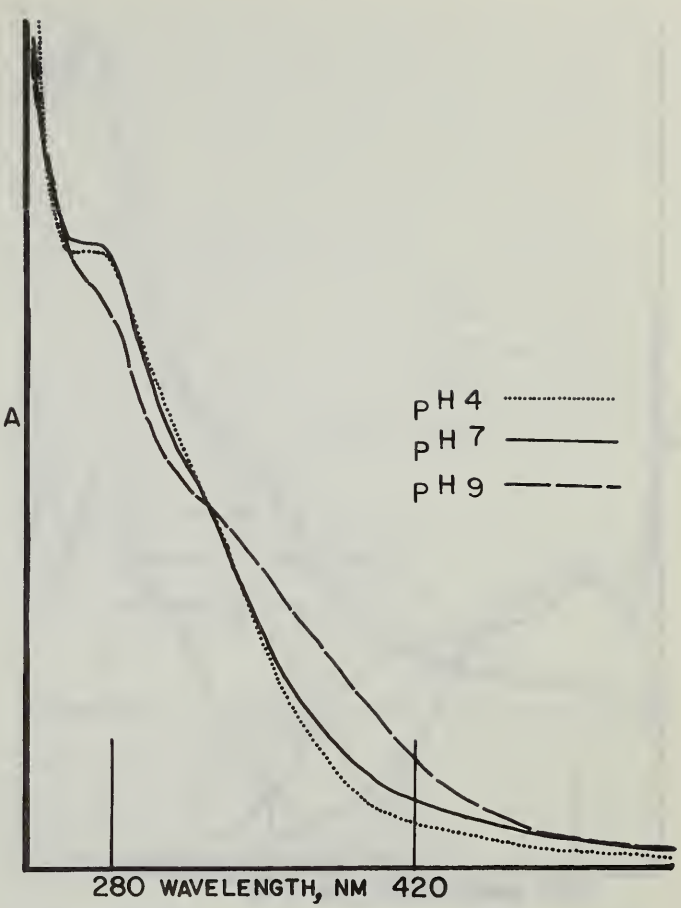

Figure 1. Spectrum of Molasses

in naturally occurring colorants such as apigenin. The hot water extract of cane leaves may be such an example, since a minimum of sugar degradation would be expected in its preparation.

The colorant isolated by eluting a Sephadex G-10 column containing adsorbed molasses colorant with water (Figure 2) has a spectrum very similar to that of the leaf extract (Figure 3), or of an affined raw sugar. Generally, a comparison of various isolated colorants or of source material for their isolation shows that the spectra of samples of high I. V. are similar in shape. Although the spectrum of apigenin (Figure 4) appears to be significantly different, the general shape of spectra of pH-sensitive sugar colorants is similar to a composite of the apigenin spectrum and that of a pH-insensitive substance such as the first fraction of a gel-filtration (Ref. 4, p. 91).

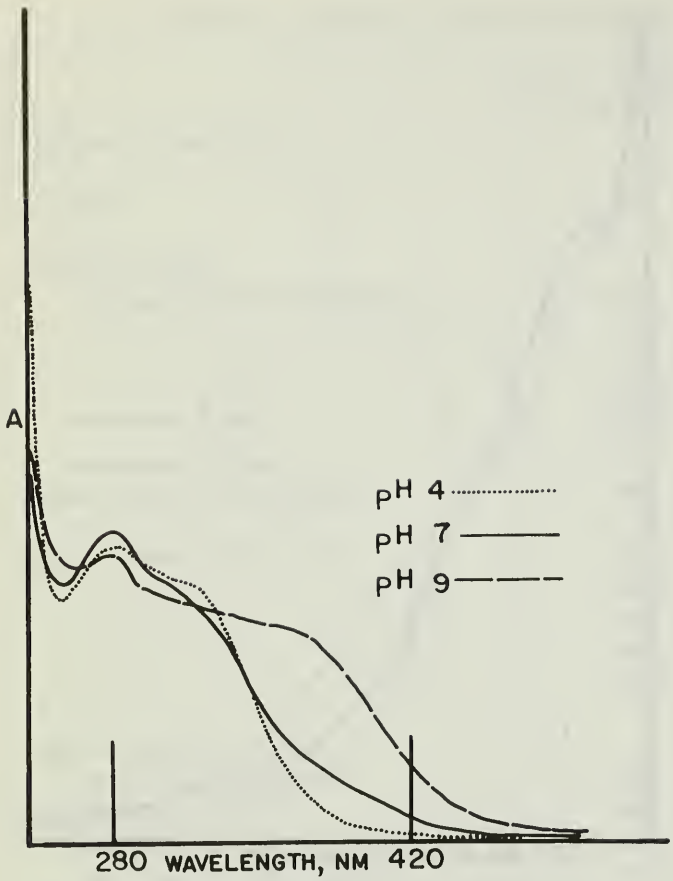

Figure 2. Spectrum of molasses colorant adsorbed on acidic Sephadex G-10 and extracted with water

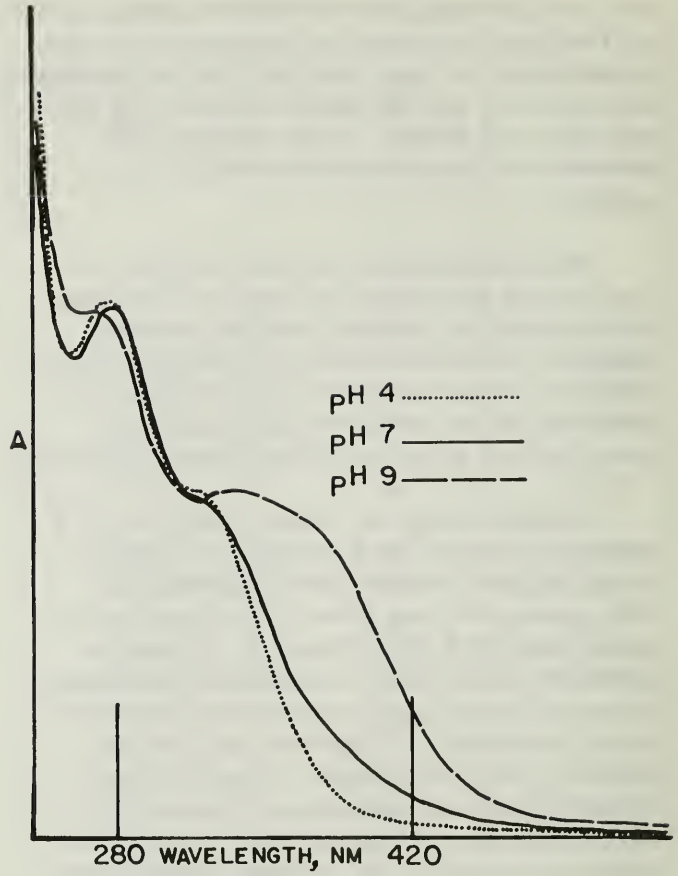

Figure 3. Spectrum of a hot water extract of Dried Cane Leaves

The last parameter we are considering is the wavelength at which the maximum pH sensitivity occurs. This approximates the wavelength of maximum absorption, under alkaline conditions, for the colorant responsible for pH sensitivity. It is obtained from a graph of the difference between the pH 9 and pH 4 spectra, as in figure 5.

The wavelength of maximum pH sensitivity (λ max) would be expected to vary widely among pure compounds, even within a given class such as the apigenin series. The constancy of λ max among the colorant sources listed at the top of the table suggests that there is little variation among the samples in the composition of the pH sensitive colorant. The higher value for apigenin (390 compared with 380-385) suggests that free apigenin is not a significant contributor to sugar colorant. However, the λ max for isolated colorants ranges from 360 to 395. Examples of these extremes are shown in Figure 5. This variation shows that in some colorant isolations there has been selective recovery of particular colorants.

In the case of colorants of low I. V., the difference in absorbance between pH 9 and pH 4 was too small to provide significant data for evaluation of λ max.

The relationship between the difference spectrum (A_{pH9}-A_{pH4}) and the I. V. (A_{pH9}/A_{pH4}) should be noted. The I. V. is dependent on the ratio of pH-sensitive to pH-insensitive colorant, but is independent of the concentra-

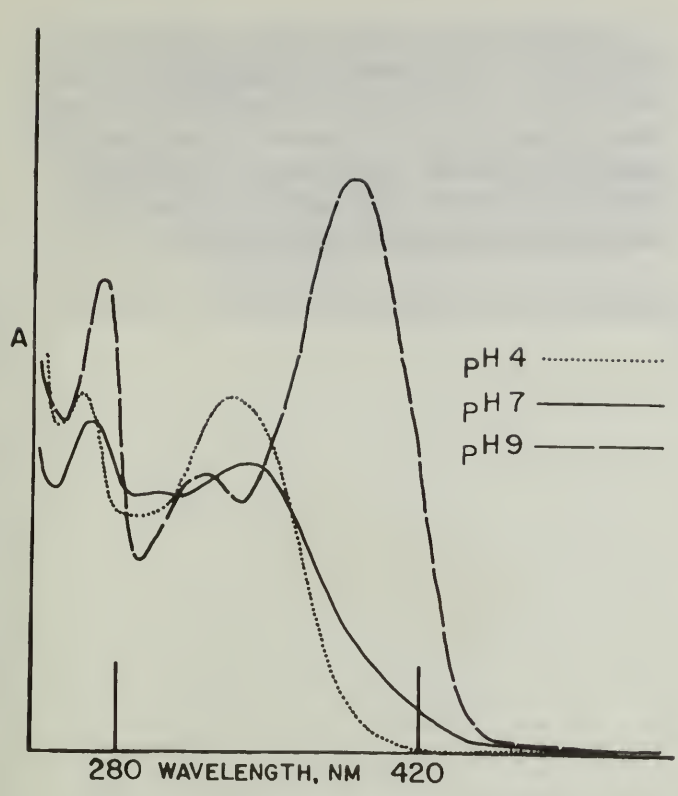

Figure 4. Spectrum of apigenin

tion of the solution. On the contrary, the difference spectrum is independent of the ratio of pH-sensitive to pH-insensitive colorant, but its intensity depends on the concentration of pH-sensitive colorant, and therefore on the concentration of the solution. The maximum I. V. of sugar colorant solutions occurs at longer wavelengths than that at which the maximum (A_{pH9}-A_{pH4}) occurs.

Electrophoretic Analysis

The analysis of complex electrophoresis patterns requires careful interpretation. The rate of migration of individual components may vary for several reasons. Although an attempt was made to reproduce conditions among several tests, some variables were beyond control. The rate of migration appears to be temperature dependent. Non-reproducible temperatures are due to variations in the rate at which heat is produced during electrophoresis. This, in turn, results from variations in conductivity of the paper which is

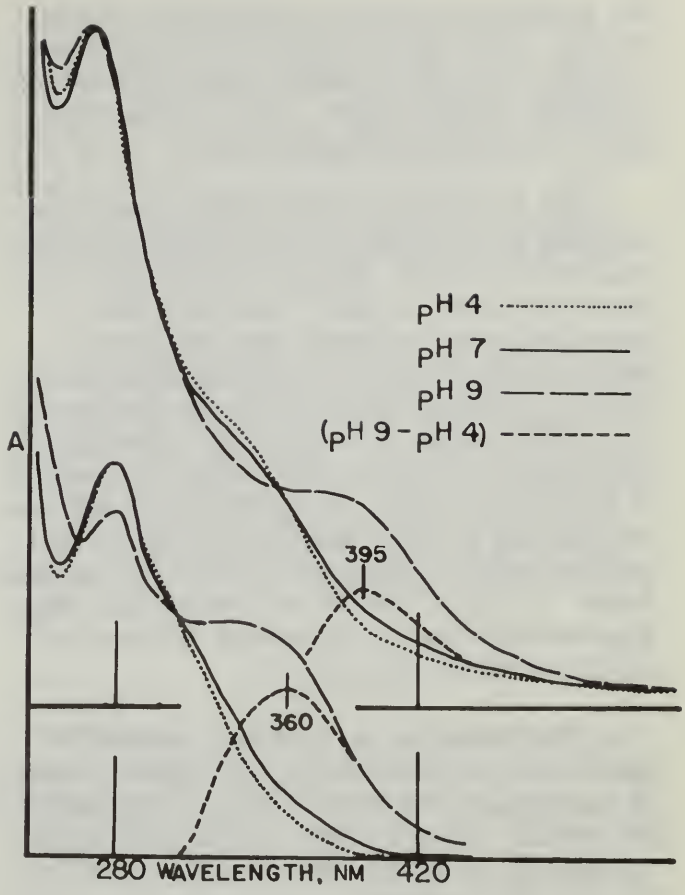

Figure 5. Upper Curves:
Spectrum of colorant slowly eluted during fractionation of molasses on Sephadex G-10

Lower Curves:
Spectrum of molasses colorant adsorbed on bone char and extracted with isopropyl alcohol

dependent on the amount of residual buffer left in the paper after blotting.

Much of the difficulty encountered from temperature variations was avoided by comparing samples on the same pherogram. Even here, however, rates of migration were found to vary from causes inherent in the samples. One of these causes is a variation in the solids content of the samples. A particular colorant migrates more slowly when obtained as an eluate of an acidic Sephadex gel column than when present in

the subsequent alkaline eluate of the same column. The acidic eluate has a lower absorption than the alkaline eluate, indicating a higher solids content. This can account for the decreased migration rate.

Not all of the colored components in a mixture are resolved as discrete visible or fluorescent spots. Some colorants are found as brown streaks. Not only may these and other colorants not fluoresce, but they may also quench the fluorescence of other substances coincident on the paper. It is also worthy of note that the intensity of fluorescence tells us little about the quantity of colorant present, since relatively low concentrations of many substances tend to appear as bright spots under ultraviolet illumination. Further, due to self quenching, the fluorescence may decrease as the concentration increases.

The streaking of colorants without the appearance of discrete or fluorescent spots is apparent in the pherograms of high molecular weight colorants such as those obtained by dialysis or as the first fraction from a gel filtration column.

Streaking and smearing of the spots was also apparent in the second and third gel filtration fractions; in the second because of a high solids content and in the third possibly because of a high ash content. Crude colorant mixtures such as raw juice and molasses tended to produce excessive streaking although several discrete fluorescent spots were discernable.

Some of the components were initially observed as distinct visible or fluorescent spots which faded after the paper had dried. In some instances the spots became no longer discernable. Visibly bright yellow spots faded within hours. Yellow or green fluorescent spots faded slowly. Examination of old pherograms occasionally showed only faint streaks. This may be evidence of chemical instability of some colorants resulting from exposure to light or oxygen.

Examples of pherograms are shown in Figure 6. The photograph illustrates what can be seen by viewing with ultraviolet light, except that spots of relatively low intensity are not apparent. Positions of maximum visible color are indicated by yellow dots along the edges of the pherograms.

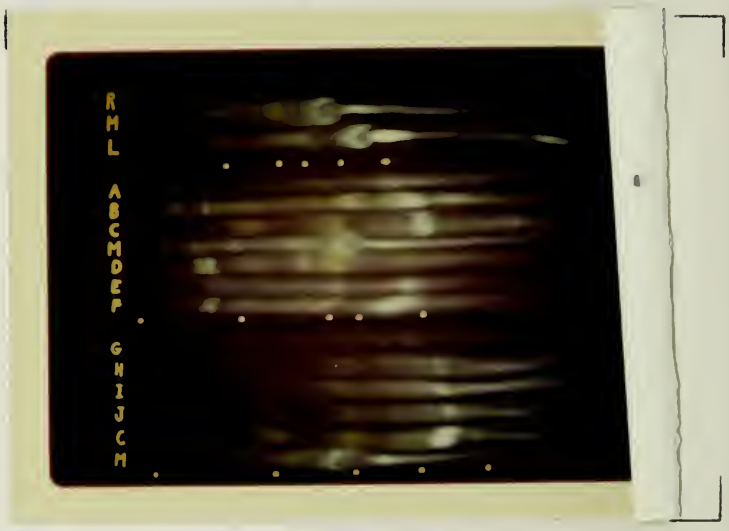

Figure 6. Color Photograph of Pherograms Viewed by Ultraviolet Light

Upper Pherogram - Colorant Sources
- R Raw Juice
- M Molasses
- L Leaf Extract

Middle Pherogram - Isolated Colorant Fractions
- A Lead Acetate Precipitate
- B Ammonia Extract of Colorant Adsorbed by Sephadex
- C Alcohol insolubles precipitated at pH 8.7
- M Molasses
- D Ammonia Extract of Non-ionic Resin XAD-2
- E Aqueous Pyridine Extract of Spent Char
- F Slowly Eluted Colorant from Sephadex gel filtration

(Legend continued next page)

Lower Pherogram - Effect of pH on Precipitation of alcohol - Insoluble Colorant

G Alcohol insolubles precipitated at pH 4.4
H Alcohol insolubles precipitated at pH 5.4
I Alcohol insolubles precipitated at pH 6.4
J Alcohol insolubles precipitated at pH 7.5
C Alcohol insolubles precipitated at pH 8.7
M Molasses

Yellow dots indicate position of visibly yellow colorants

In the upper pherogram of Figure 6, colorant sources are compared. Raw juice contains yellow fluorescent substances common to molasses and the leaf extract. The latter, however, contain in addition, several components which migrate more rapidly than those of the raw juice. Most prominent of these fast migrating compounds is a blue fluorescent substance, visibly yellow, and common to molasses, the leaf extract, and to most of the colorant fractions shown in the other pherograms. Its presence in the leaf extract and molasses but not in raw juice (from hand-cut cane) may support the contention that some of the color with which the refiner must deal is taken in with the trash during harvesting.

The middle pherogram of Figure 6 compares representative samples of several isolated colorant fractions. Omitted were examples of colorants which were not resolved into discrete spots. These include non-dialyzable colorant and the first fractions of colorant eluted from a Sephadex column during gel filtration.

In general, where samples could be resolved into distinct components, the same colorant spots appeared in samples isolated by different methods. The fast-migrating colorant mentioned above, visibly yellow but blue under ultraviolet light, was common to molasses, the leaf extract, Sephadex gel eluate, alcohol insolubles, and char extracts. It was not seen, however, in extracts of the non-ionic resin XAD-2. The resin extract, however, had other components in common with most of the other isolated colorant fractions.

The bottom pherogram of Figure 6 shows the variation in composition of alcohol-insoluble colorant produced by precipitation at increasing pH. It is apparent that as the alkalinity is increased, the content of colorant in the alcohol precipitate which produces discrete spots is also increased. These spots can be seen by both visible and ultraviolet light.

SUMMARY

Colorant rich fractions can be obtained from molasses, more or less free of the bulk of colorless sugars and other substances, by several techniques. The spectral and electrophoretic analysis of the fractions obtained by these techniques indicate that a large number of components are present in most isolated colorant fractions as well as in the source of colorant.

The proportion of different colored compounds in the various fractions varies, depending on the method of isolation. For the study of a particular colorant type, some methods are preferred over others; an awareness of the selectivity of each technique should be a guide to the investigator studying the contribution of different colorant types in raw sugar or other materials.

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DISCUSSION

C. W. Davis (Colonial): I gather that many of these colorants are related to apigenin. You showed the absorption curve for apigenin to have a fairly well defined maximum in the near ultraviolet, and yet there does not seem to be a corresponding maximum in the absorption curve for your expected colorants. Would you care to comment on this, please?

F. G. Carpenter (S. R. R. L.): The apigenin related colorant bodies, these flavones, all come from the cane -- primarily from the rind and leaves. The curve shown was for pure apigenin. But all of these other colorants are substituted apigenin, and you can expect that substituted apigenin compounds will each have a slightly different curve. Now, mix many of them together-then you no longer get one maximum, but a general smooth curve -- perhaps with a few wiggles in it.

K. Schoenrock (Amalgamated): I wondered about this absorptivity term, and I wonder if it relates to a comparative quantitative measurement of the colorants?

N. H. Smith (C&H): The absorptivity is essentially the attenuation index. To find it, divide the absorbance of the solution by the product of path length and concentration. I used grams per milliliter as the units of concentration.

K. Schoenrock: Is this grams of the colorant?

N. H. Smith: No, grams of the solid material, and the solid material is not 100% colorant. That's why we get large variations. In determining attenuation index of a granulated sugar, you use grams of sugar per ml. as your solids. You are measuring the absorbance of the colorant but using the weight of the sugar.

K. Schoenrock: Then this is on dry substance?

N. H. Smith: Yes.

K. Schoenrock: How did you test for completeness of stripping from the ion exchange resin?

N. H. Smith: I didn't. I was not concerned with what stayed on. I was only interested in getting samples of material by various methods. Hopefully by comparing samples from various methods, I could determine which method would be most useful for further study. I was not concerned with getting quantitative recovery.

K. Schoenrock: Another thing that I wondered about is, did you have any spectra on refined sugar? How did that compare spectrally with the colorants that you got from molasses and leaves?

N. H. Smith: Depending upon the liquor that you are boiling, the spectrum of refined sugar may very well be similar to that of a raw sugar. That is, it will have a similar pH sensitivity. My paper presented at our 1964 session discussed the effects of refining steps on some of the spectral properties of sugar.

B 2

THE ISOLATION AND PROPERTIES OF SUGAR COLORANTS

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INTRODUCTION

The variation in the properties of the coloured impurities of raw sugars is a major problem in sugar refining. Broad spectrum decolorizing agents are required, which usually have low decolorization capacities. Decolorization is consequently an expensive and limiting process in refining.

Ideally, the purification process should employ methods appropriate to the properties of the impurity to be removed. An example would be the application of anion-exchange resins to the removal of anionic colorant. This could offer significant economic advantages over the use of a carbonaceous adsorbent. However, properties other than the anionic function of colorant have presented difficulties which have delayed the wide adoption of ion-exchange decolorization.

A study of the properties of the colorant found in raw sugars and that formed during refining has been undertaken. This has involved (1) the development of methods of concentrating and isolating the colorant, (2) the separation of the colorant into fractions homogeneous with respect to a selected property, (3) relating the chemical and physical properties to the structure, origin and behaviour of the colorant.

For this purpose, colorant is distinguished from the particulate matter present in raw sugar solutions, frequently included in colour measurements, even if the suspended impurity is itself coloured. This appears to be either colorant insoluble in the solution, or colorant adsorbed by insoluble impurities, such as starch or protein.

The methods of colour measurement used, and the designation of colour is in accordance with the proposals made previously (1). Namely, that colorant concentration (units/ml.) is defined as the absorbance of 1 cm. depth of solution at pH 7.5 at 455 nm.

Isolation of the Colorant

In the isolation of the colorant, which may be present in solution in very low concentration, as in refined sugar syrups, it is necessary to avoid, as far as possible, selective separation, until the properties of the whole colorant have been established. Conditions which could lead to chemical changes should also be avoided. Two methods were finally selected, which approached most closely to this ideal, and which would be generally applicable.

The hydrated polystyrene resin, Amberlite XAD-2 will retain all colorants, studied so far, irreversibly at low pH. Sugars and inorganic salts are not retained, though some organic acids including amino-acids are found to be partly adsorbed. At pH 2 and below some colorants tend to precipitate from solution. The procedure adopted is a compromise which allows the recovery of around 95% of the original colorant.

Amberlite XAD-2 resin is packed in water in a 2 cm. diameter column to a height of approximately 40 cm. The resin is washed with methanol until the effluent is free from dissolved material from the resin. This is followed by washing with aqueous hydrochloric acid (1 mN) until all methanol has been displaced. The coloured solution, which has been filtered if necessary, adjusted with hydrochloric acid to pH 3, is pumped (at 1 ml./minute) upward through the column. This is followed by 1 mN. hydrochloric acid until the eluate is free from sugars. The column is washed free from chloride using

distilled water. Some desorption of colour occurs at this stage. The colorant is finally desorbed by washing with methanol in downward displacement.

The solvent is evaporated at room temperature, and the residue is dried in vacuo. The product is termed the Y-fraction. That retained on the resin, the Z-fraction, may be eluted from the resin using methanolic hydrochloric acid (10 mN). The colorant is precipitated from the acidic methanol by the addition of benzene. The precipitate is washed with ether and dried in vacuo.

An alternative method, avoiding the need for acidic conditions, involves the precipitation of the anionic colorant at pH 7.5 with an aqueous dispersion of dioctadecyldimethylammonium chloride of hexadecyltrimethylammonium bromide (C. T. A. B.). The precipitate is washed with water and dried in vacuo.

The excess of dioctadecyldimethylammonium chloride may be removed from the dried precipitate by continuous extraction at room temperature with petroleum ether (bp 40-60°), though this is not necessary. The residue is dissolved in ethanol and the solution, in the case of purely anionic colorant, is passed over a column of Amberlite 200 (H^+ form) packed in ethanol. Evaporation of the effluent at room temperature leaves the colorant as the free acid.

Alternatively, the coacervate (precipitate) is dissolved in ethanol and the potassium salt of the colorant is precipitated by the addition of an ethanolic solution of potassium bromide. This is necessary for amphoteric colorant which would be retained by Amberlite 200.

The C. T. A. B. precipitate may be similarly treated in methanol solution, from which the calcium salt of the colorant may be precipitated by the addition of a methanolic solution of calcium chloride.

Properties of the Colorant

The predominant proportion of the colorant does not have a definite or constant molecular composition or reproducible properties. Consequently, the usual criteria of purity cannot be applied, and no attempt has been made to obtain a pure fraction.

The relationship between variation in different properties has been examined with the object of relating these to the solution properties and molecular structure of the colorant.

Absorption Spectra - Visible

The visible absorption spectrum is the most readily studied property of colorant. A singular feature is the consistency of the relationship between absorbance and wavelength, namely $A_\lambda \cdot \lambda^n = k$. This is independent of the concentration of the colorant, and the wavelength index is a characteristic property. This is most conveniently measured as the N-value, which is defined as one hundred times the square of the ratio of the absorbance of the solution at 520 to that at 455 nm. (1). Its value normally lies between 5 and 50.

This parameter is related to the proportion and extent of conjugation of unsaturated centres in the colorant polymer. The probability of extended conjugation increases with increase in polymer length. Consequently, N-value is an indication of colorant molecular weight, low N-value being associated with low molecular weight.

Determination of the specific absorbance of isolated colorant from different sources, shows that the colorant has a similar specific absorptivity at 455 nm. irrespective of type or origin (Table 1). This is of course not true at other wavelengths.

This indicates that the higher colour development from reducing sugars in the pres-

Table 1.

Source	Glucose degradation	Maillard Reaction		Raw Cane
		Glycine	Lysine	
Specific Absorptivity	2,950	2,390	2,120	2,420
Wavelength exponent	5.13	4.26	5.25	4.75
N-value	25.4	32.9	24.6	23.1

ence of amino-acids is a consequence of more efficient conversion into coloured products than in the thermal degradation of reducing sugars.

ULTRA-VIOLET

The ultra-violet spectrum of the colorant tends to be uninformative, owing to the intense absorption at the shorter wavelengths due to ethylenic and carbonyl unsaturation. However, in raw sugars, superimposed on the smooth curve of the spectrum are inflexions at around 265 nm. and 234 nm. Removal of the colour shows that these absorptions are due to the presence in the solution of at least three colourless intermediates. That at 234 nm. is due to 5-hydroxymethyl furfural, while the characteristic absorption at 265 nm. (Fig. 1) results from the superimposition of the spectra of two non-ionic dicarbonyl colour precursors, showing separate absorption maxima at 255 and 272 nm. The former is an unstable volatile white crystalline solid (mp 82° decomp.) with a characteristic odour. It is in equilibrium in solution with the second involatile component. The structures of these compounds have not yet been elucidated, though the infra-red spectrum of the volatile component supports the structure shown at right.

INFRA-RED

The infra-red spectra of colorants isolated from diverse sources and having

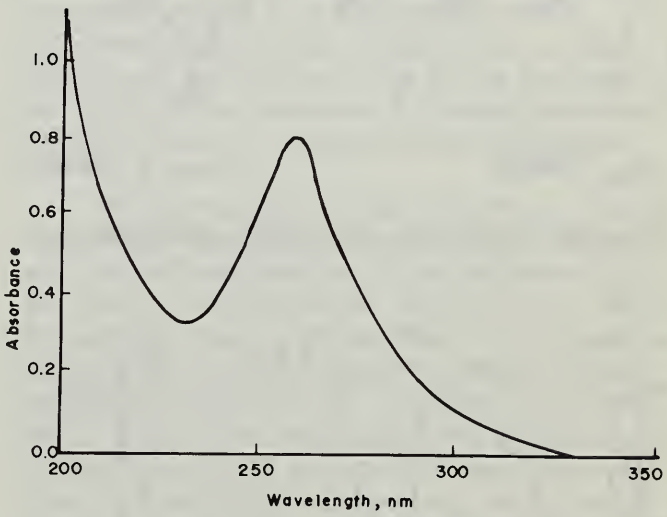
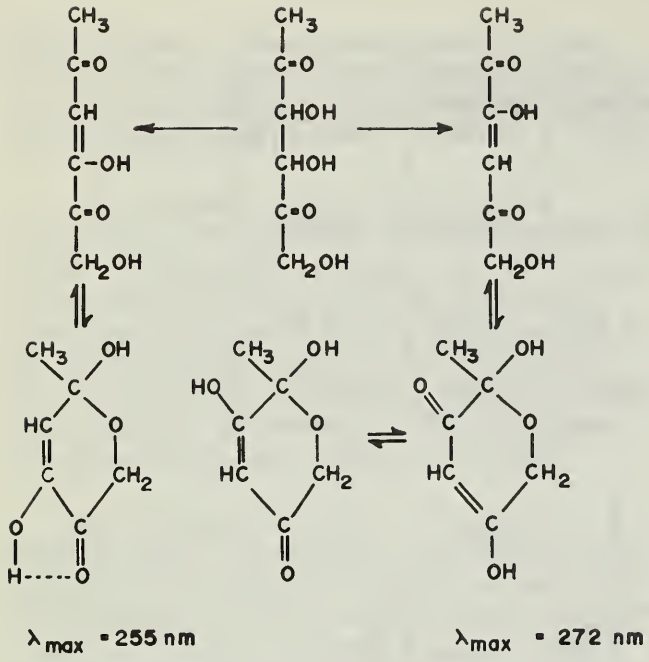


Figure 1. Absorption spectrum of colour precursor

widely dissimilar properties are remarkable in being closely similar (Fig. 2). The resolution of the spectra has not been improved by fractionation of the colorant. This would indicate that the absorption bands suffer displacement owing to differences in the molecular environment of particular bands in the same molecule.

The presence of a weak aliphatic C-H absorption and a broad hydroxyl band in the spectrum resembles that of carbohydrates. The presence of ethylenic double bond and the carboxyl group are clearly indicated. The carboxyl absorption is characteristically split in the spectrum of the calcium salt. The complete absence of aromatic C-H ab-



Proposed structures for colour precursors

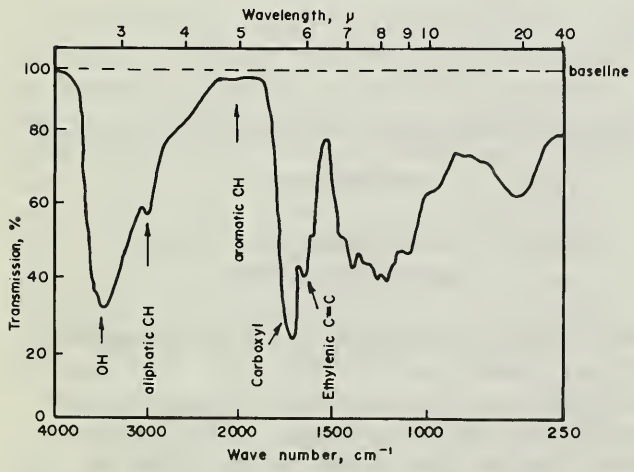


Figure 2. Infra-red spectrum of anionic colorant

sorption, consistent with the ultra-violet spectrum, supports the assignment of an aliphatic polymeric structure to the colorant.

The methyl ester of colorant is readily prepared by methylation with diazomethane. The ester, unlike the original colorant, is soluble in methylene chloride, as is also the acetate. The infra-red spectra in this solvent do not show improved resolution. The presence of the vinyl carboxylic ester (-C=C-CO-OCH_3) and of the enol acetate (-C=C-O-CO-CH_3) is confirmed. Maillard colorant also shows an absorption which has been attributed to the amide group.

Charge-type

A high proportion of the colorant of raw sugar and refinery molasses has been shown to be anionic. However, colorant formed during the degradation of sugars in the presence of amino-acids (Maillard reaction) may contain amine nitrogen, which at low pH exhibits cationic properties. Consequently, colorant may also be amphoteric.

Separation of the two types of colorant may be effected at low pH (2) when ionisation of the carboxylic acid groups will be suppressed and the cationic function of the colorant will be ionised. Using the macroreticular Amberlite 200 cation exchange resin in methanol, matrix adsorption is suppressed. On passing a solution of the colorant in methanol at pH 2 through a column of the resin (H^+ form) only the cationic fraction is retained. The cationic colour may be displaced with aqueous alkali (0. 1 N), the elution of the amphoteric colour being according to its basic strength. By this method an ionic profile of the colorant may be obtained (Fig. 3).

Although the presence of cationic centres on the colorant polymer does not significantly affect the spectral characteristics either in the visible or infra-red, other properties which depend on charge interactions are radically altered. Obviously the electrophoretic behaviour will reflect the differences in net charge at a particular pH, though charge density will also be important.

More subtle consequences of charge interaction are evident from a study of anion-exchange resin decolorization. A purely anionic linear polymer at neutral pH will

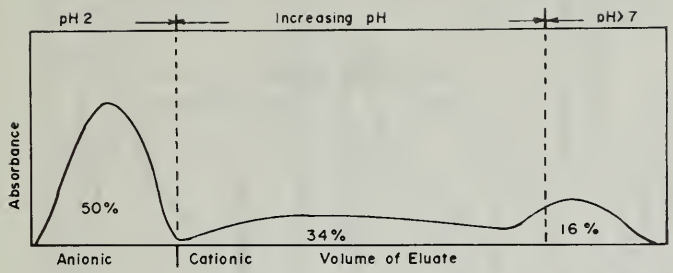


Figure 3. Molasses Y-colorant composition as a function of basic strength

exist in solution as an extended chain owing to charge repulsion of neighbouring anionic centres. If, however, mutual repulsion is replaced by attraction, by interposing cationic centres along the chain, then the molecule collapses becoming roughly spherical and the net anionic charge is reduced. Finally, if an excess of strongly basic groups are present mutual repulsion of positive charges predominates and the molecule is again extended.

This is demonstrated by the behaviour of a strongly basic colorant in the presence of formaldehyde which reacts reversibly with a primary amine converting it to the weakly basic methyleneimine. In this form it is retained by a styrene based anion-exchange resin but not in the strongly basic form.

Net Anionic Charge

Ion-exchange resins show a strong tendency towards irreversible retention of colorant, owing to simultaneous adsorption by the matrix. While the recovery of colour from cellulose based anion-exchangers is incomplete, non-ionic adsorption, especially that due to hydrogen bonding, may be suppressed by working in aqueous urea (8 M.) or dimethylformamide (50%) solution.

Using a column of an anion-exchange cellulose, Whatman DE - 32 in 50% aqueous dimethylformamide buffered at pH 7.5, anionic colorant may be retained by ion-exchange alone. Elution with increasing concentrations of sodium chloride results in desorption of the colorant in order of increasing net charge.

It was found that anionic colorant of low net charge, also had a low molecular weight, and low N-value. Its infra-red spectrum was unchanged. It was also found that it is this fraction which is most readily eluted from an anion-exchange resin, as would be expected.

Anionic Charge Density

Polymeric anions are precipitated from solution by long chain alkyl quaternary ammonium ions. Similarly polymeric cations are precipitated by anionic surfactants. Amphoteric colorant is found to be precipitated from aqueous solution at the appropriate pH by either hexadecyl trimethylammonium bromide or by sodium dodecylsulphate.

The insolubility of the coacervate with a quaternary ammonium surfactant in the presence of sodium chloride is an indication of the charge density on the polyanion (2). When the anionic charge arises from the ionization of acids of different basicity, charge density will be a function of pH. Colorant derived from the thermal degradation of reducing sugars displays a progressive increase in charge density with increase in pH up to 10. This characteristic is very much less pronounced in the amphoteric Maillard colorants. This is interpreted as indicating the participation of enolic ionization in the former case, while in the latter potential enolic groups have reacted with amines and are no longer ionizable. This would account for the indicator effect observed with anionic colorant but not with Maillard colorant.

The procedure followed was to titrate a solution of the colorant (4.5 units in 25 mls.) at the appropriate pH contained in a 4 cm. Spekker cell with 0.1% C. T. A. B. The attenuation of the solution was measured, after stirring for one minute after the addition of reagent, in the Spekker absorptiometer using a red filter. The salt effect was studied in a similar manner, the suspension of the C. T. A. B. - colour coacervate being titrated with sodium chloride solution.

The results obtained with a purely anionic and a purely amphoteric colorant are shown in figures 4, 5, and 6.

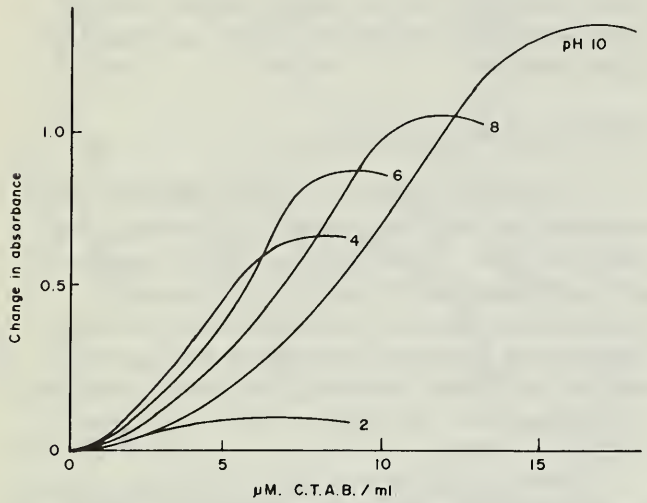


Figure 4. Precipitation of anionic colorant as a function of pH

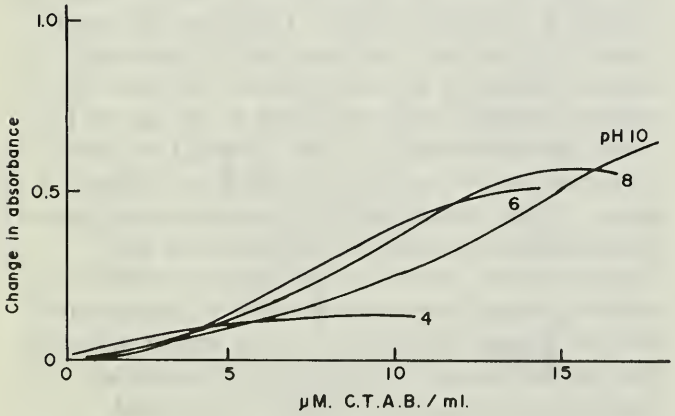


Figure 5. Precipitation of amphoteric Maillard colorant by C. T. A. B. as a function of pH

Molecular Weight

The molecular weight average and distribution of colorant is a property which would be expected to be associated with the observed physical characteristics of different colorants. So far, homogeneous fractions have not been separated, so that the usual

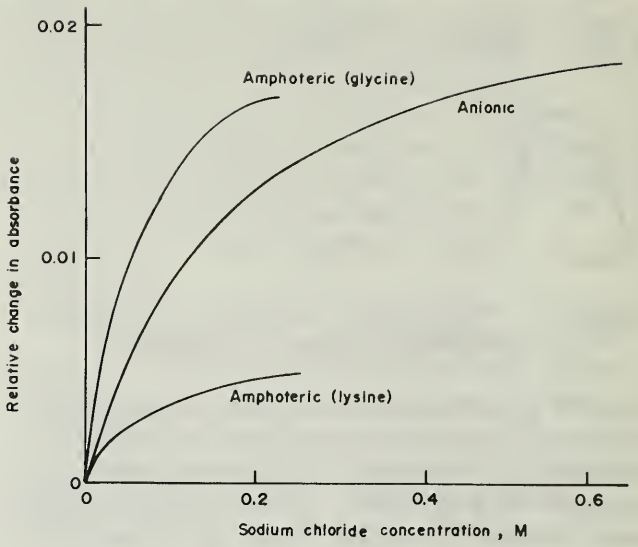


Figure 6. Solubility of colorant - C. T. A. B. coacervates as a function of salt concentration

methods of molecular weight determination are not applicable.

Gel permeation is a technique which has previously been applied to the fractionation of sugar colorant according to molecular weight, (3). However, adsorptive retention of colorant by the gel matrix has led to doubt concerning the interpretation of the results. Some workers have concluded that the technique is inapplicable to sugar colours, (4). Nevertheless, this method would be of value in indicating relative molecular weight distribution, where a continuous spectrum of molecular sizes is present, provided that adsorption is avoided.

In relating a molecular weight scale to the observed partition coefficient in gel permeation, it is necessary to recognize that molecular shape is an important factor determining diffusion rate. The relationship is, therefore, likely to depend on the colorant type present, and on the molecular environment. Consequently, even in the absence of adsorptive retention, colorant will permeate at a rate which is not necessarily directly related to molecular weight.

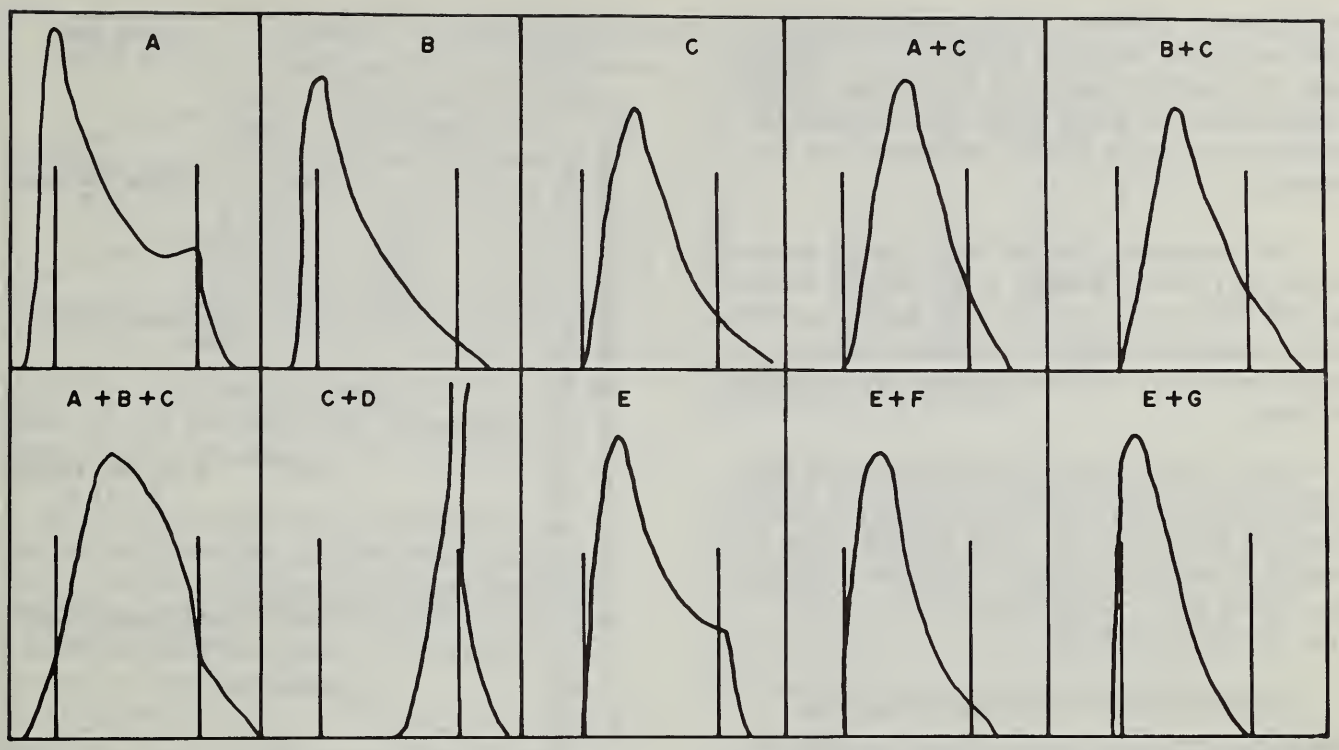


Figure 7. Gel Permeation of anionic colorant on Sephadex G. 25.
Eluting Solvent: A, 1% Pyridine; B, 0. 1M. Bicarbonate buffer (pH 10. 2);
C, 1M. Sodium chloride; D, Hydrochloric acid (pH 2. 4);
E, 0. 01M. Triethanolamine Buffer (pH 7. 5); F, 1. 5M. Urea;
G, 8M. Urea

The effects of molecular environment, adsorptive retention and molecular shape are illustrated in the series of curves (fig. 7), obtained using the same colorant but in different solutions on Sephadex G. 25. It was tentatively decided that the use of 8M. urea buffered at pH 7. 5 with 0. 01M. triethanolamine as the developing solvent would give the best indication of molecular size distribution.

It is also to be expected that using two gels of different size discrimination (for example Sephadex G. 25 and G. 50), where the molecular size ranges overlap the same distribution should be obtained. Using this criterion it was found that the best agreement was obtained if anionic colorant is regarded as an extended chain similar to dextran, while amphoteric Maillard colorant shows analogies to a globular protein.

The relationship between molecular weight (M) and partition coefficient (K_D) for a linear molecule in Sephadex gel permeation is best given by Porath's equation (5):

$$K_{D^{1/3}} = a\, M^{1/2} + C.$$

On the other hand, a logarithmic equation is most appropriate to Maillard colorant, and is of the form:

$$K_D = B \cdot \log M + C.$$

The interpretation of partition coefficients is

consequently difficult when a mixture of colorant types is being examined. Nevertheless, the determination of molecular weight distribution can be of value even though the precise molecular weight equivalent is uncertain.

For example, two strongly basic anion-exchange resins, Kastel A 501 D and Amberlite XE 258, were used to decolorise a solution of anionic colorant. Neither resin effected complete decolorization: the question was why.

The input colour had N-value 22.3, the effluent colour from A 501 D, N=27.2 and from XE 253, N=17.5. The resins were regenerated with 2N. sodium chloride solution. The eluate from A 501 D had N=17.1 and from XE 258, N=20.6.

Gel permeation chromatographs on Sephadex gave the results shown in Fig. 8. The significant difference between the resins showed clearly that their selectivity for colorant is related to molecular size.

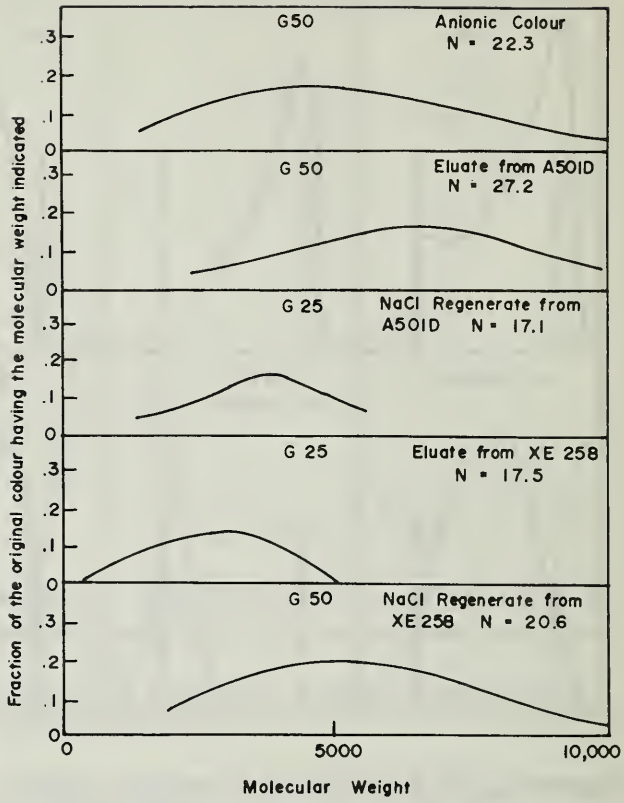


Figure 8. Molecular Weight distribution curves from Sephadex Gel Permeation of anionic colour retained or rejected by Kastel A 501 D or Amberlite XE 258 ion exchange resin

Alumina Adsorption

An empirical but reproducible method of separating colorant, is based upon its adsorption on active alumina. The following procedure is used.

Neutral alumina (10 ml. 'Camag' M. F. C., 100-200 mesh) is shaken with water, allowed to settle for 5 minutes and the suspended fines decanted. The remaining material is packed in a 1 cm. diameter column. A volume of colorant solution containing approximately 100 colour units is run onto the column (0.3 ml./minute). The column is washed with water (1 ml./min). The first 10 ml. eluate is discarded and the next 50 ml. collected. Elution is continued with tartaric acid (0.1M., 100 ml.) and the eluate collected. The colour in each eluate is measured at 455μ, after membrane filtration and adjustment of pH to 7.5. The proportion of the original colorant in each eluate solution are calculated, and that retained by the alumina obtained by difference. The fractions are designated A, B, and C.

A - Not retained
B - Retained but eluted with tartaric acid
C - Not eluted with tartaric acid

So far, the property which determines to which fraction a colorant belongs has not been established. C colorant is of high molecular weight and is formed from A and B colorants during a process of ageing. It is also the fraction of colorant which is specifically removed on phosphatation, neither A nor B being affected.

The ageing of colorant is illustrated in table 2. A solution of glucose is subjected

Table 2. --Change in colorant composition on ageing

Age	Original N-value	Fraction A %	Fraction A N	Fraction B %	Fraction B N	Fraction C %	Fraction C N (calc)
1 day	18.6	44	12.3	48	21.2	8	37.5
8 days	18.5	36	11.5	42	18.5	22	30.0
21 days	22.0	30	12.4	35	19.9	35	32.3
6 months	24.2	25	12.7	27	18.0	48	33.5
8 months	22.4	27	13.7	25	18.1	48	30.0

to thermal degradation at pH 9.5. The composition of the solution after increasing periods of time is shown.

An application of this procedure is in obtaining evidence for colour generation during a process such as charring, in which colour is simultaneously being removed. An increase in the A component is strong evidence for colour formation.

Solubility

The solubility of different colorants in organic solvents, in particular alcohols, depends on whether the colorant is in the form of a salt or the free acid. Generally, the free acid is the more soluble, so that the proportion of a colorant which can be extracted from aqueous solution by, for example, amyl alcohol increases with decrease in pH. The solubility of the colorant in an alcohol decreases as the homologous series of alcohols is ascended. As would be expected, amphoteric colorant is less soluble as the proportion of basic groups increases.

Consequently, a crude fractionation of colorant can be effected by precipitating with an alcohol. 76% of the colour of a refinery 1st crop syrup was precipitated with methanol. The precipitated colorant contained all the original Z-colorant (20%) and two thirds of the original C-colorant (54%) fraction.

It is interesting that in the free acid form, glucose Y colour is insoluble in water but soluble in methanol, Maillard (lysine) Y-colour is soluble in water but insoluble in methanol, and Z-colour is soluble in water and in methanol.

Structure of Colorant

Although the detailed structure of sugar colorant has not been established, an outline of its main structural features is discernible. The close similarity of the spectra, in the ultra-violet, visible and infra-red regions, of the colorant, irrespective of origin or fractionation indicates that the main chromophore is a simple repeating unit.

The progressive unsaturation suggests a facile dehydration with the formation of unsaturated bonds. This indicates the presence of hydroxyl groups β to an electron withdrawing group, probably carbonyl. The carboxylic acid groups are almost certainly the product of a benzilic acid type rearrangement, probably occurring after polymerization.

An aldol type condensation is the most likely polymerization mechanism which can occur readily in dilute aqueous solution. In the Maillard reaction, nitrogen uptake follows colour formation, and is independent of this. The lower anionic charge density of amphoteric colorant, and the negligible dependence of absorbance on pH (indicator effect), suggest carboxyl-amine condensation, competitive with benzilic acid transformation, and enolisation.

The colorant is thus deduced to be a linear polyaldol condensation product of a polycarbonyl intermediate, which has undergone dehydration and internal oxidation reduction. Cross-linking of the linear chains is believed to give rise to the Z-fraction of colour.

The properties of the colorant are determined by the degree of unsaturation and hence the hydrophilic-hydrophobic balance, the molecular weight and degree of cross-linking, and the ratio of anionic to cationic groups of the polymer.

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DISCUSSION

A. Clarno (Savannah): You refer to evidence of the presence of a color precursor. Are you implying that all color formed is derived from this intermediate?

K. J. Parker (Tate and Lyle): No, not really. I think the term "color precursor" covers quite a large number of substances, for instance sugar itself -- sucrose -- is a color precursor insofar that it can undergo inversion, producing reducing sugars which are primary precursors of color. What I was really meaning was that this particular compound which we have isolated seems to be an intermediate in color formation. We have a lot of evidence that the different routes by which color is formed appear to go via this intermediate. There are quite a number of other substances which can be regarded as, and probably are, major color precursors -- such as dihydroxyacetone and invert itself really, so I'm certainly not suggesting that there is just one precursor of color and that this is it.

A. Clarno: Color formed in raw sugars by the Maillard reaction is predominantly in the syrup. Have you had any indication that this reaction and its resulting colors will occur in the crystal lattice?

K. J. Parker: Well, we have been studying this, and I think that the evidence that we have at the moment is rather contradictory. On the whole, I would say that probably there is no good evidence that the color is selectively retained by the lattice. But I'd really like you to wait for a final answer until we have taken this a bit further and can answer with a little more confidence.

A. Clarno: With your background of these color investigations would you care to comment on why colors are formed by the Maillard reaction?

K. J. Parker: Well, our view is that the Maillard reaction is just a specific example of a much more general reaction, leading to the formation of color. Briefly, I mentioned a precursor of color and this precursor is itself formed for instance from pyruvaldehyde. Pyruvaldehyde itself can be formed from the dealdolization reaction of deoxyhexosulose, which has been ably shown by Anet in Australia. In the early stages of the Maillard reaction, deoxyhexosulose is formed, as in the alkaline degradation of reducing sugars, by a direct route. This reaction is catalyzed by calcium ions and amino acids, or primary amines in general. Strong base amines are extremely good catalysts. This is one route and this is why one gets color formation with amino acids.

S. Stachenko (C&D): In the original part of your talk, you mentioned separating color by passage of the solution through Amberlite XAD2 and you commented that, if necessary, the solution is filtered. What do you call necessary, and if you filter, over what?

K. J. Parker: Well, if one is starting out with a raw sugar solution or something like that, and it is obviously absolutely loaded with colloidal matter, it's advantageous to

filter it. Filter it through Kieselguhr - just to get rid of the rough stuff, anyway. Particulate matter is not retained very noticeably by the Amberlite XAD-2 and if it is retained, it is filtered off or just stuck onto the beads. You will find that you won't elute it with methanol or hydrochloric acid.

S. Stachenko: You referred to a precursor that you had isolated, and indicated a melting point of about 82° C., and you also mentioned that it was volatile and had a special odor. Could you comment on the odor?

K. J. Parker: Well, I'm not very good at describing odors but I would say it smells like burnt molasses. It's not really characteristic of molasses -- a rather more burnt odor. You recognize it if you smell it but you can't describe it.

N. H. Smith: It is my experience that colorants that are prepared by alkaline degradation and in the Maillard reaction do not produce large numbers of spots on electrophoresis, and I thought it would be interesting to comment on this, because we may be talking about different types of colorants: the ones that are produced in processing, and the ones that we see as very nice colors on electrophoresis.

Another comment was on the 320 nm. absorption peak. I don't find that it's peculiar to Hawaiian raws, nor in all Hawaiian raws. Apparently high-quality raws tend to show more of this characteristic absorption, high-quality meaning good decolorization.

R. Kunin (Rohm and Haas): There is one point on which I should like to have Dr. Parker comment, and perhaps some of the others would also like to comment. Has any consideration been given to heavy metals, such as iron and copper? We have found that strongly basic anion exchange resins, which are returned to us by sugar refiners after having been used for a long period of time and are essentially spent, have a considerable amount of copper and iron associated with them, which comes off when we elute the color. Since these color bodies that you have described are potentially excellent chelating agents, I was wondering if you have determined if there are any heavy metals associated with some of your colored materials, and also what happens to the spectra of some of these materials that you've fractionated in the presence of these heavy metals?

K. J. Parker: This is a topic which I would like to discuss at length, because we have studied it in great detail. To be as brief as possible, first of all it is quite true that heavy metals, in particular, iron, are strongly complexed in sugar solution, particularly by the colored products themselves. We recognize that we haven't actually isolated products of the decomposition of reducing sugars, which products we refer to as the chromagens, which are characterized by reacting with iron ions in solution to give strong adsorption in the red end of the visible spectrum. This, of course, means that the solution turns black if you have got enough of it there. We've studied the formation of this particular chromagen, and we find that it follows quite closely the formation of color -- it is obviously closely associated with color. One interesting feature of this particular chromagen is that it is one of those compounds which is specifically removed during phosphatation, and we can get rid of it all as well as the iron. If you put iron back in the solution there is no reaction. It has been suggested that polyphenolic substances are responsible for complex formation. I've no doubt that these are present and that you do, of course, get the characteristic interaction of iron with polyphenols and some color change, but even in the absence of polyphenols you still get a color change. Also, we have no evidence of the presence in these solutions of an aromatic type of compound which could be referred to as a polyphenol. However, there are compounds of the ascorbic acid type which, of course, do react with iron to give colored products which absorb at longer wavelengths. This is, of course, characteristic of the enediol grouping, which further evidence shows

to be present in the color itself. So, this may be a chelating reaction between the color, as you suggest, and the iron. In this connection, it has been suggested in the literature that iron is a catalyst in color formation. We have shown, I think, very definitely, that this is not so. In our studies, we have found no evidence for catalysis by iron. What we have found is that in the presence of iron, even a few hundred parts per million, you get very intense color formation. But if you remove the iron from the solution, you find that the color is a product of the interaction of iron with the chromagens which are formed simultaneously with color.

SUGAR DUST EXPLOSION VARIABLES

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INTRODUCTION

Faraday in 1844 was the first scientist to establish that dust explosions could occur. He showed that coal dust could, if distributed to form a cloud in air, be ignited and burn. In 1880 a government authority, namely the Royal Commission on Accidents in Mines, admitted that airborne coal dust could give rise to violent explosions. Eventually, by the beginning of this century, dust explosions became accepted phenomena.

Most early work was directed towards determining dust ignition temperatures by blowing a known mass of dust down a heated tube. This lead to a qualitative classification of industrial dusts (1) and the identification of factors influencing explosions. These are:

1. temperature and pressure and composition of the atmosphere containing the cloud,
2. the average dust particle shape and size,
3. the degree of agglomeration of the particles,
4. the concentration of dust,
5. the ignition source temperature and
6. the energy emitted from the source.

It is generally accepted that the combustion of individual dust particles (e.g. sugar) causes an increase in the local gas volume which in turn leads to the development of a pressure wave which passes through the vessel containing the cloud. This in turn leads to the damage observed.

The velocity of the flame and the combustion wave is governed by the cloud and the individual dust particles. The pressure wave can cause an increase in flame velocity and also the dust concentration because it can bring into suspension dust that had settled out on to floors, beams, etc. In fact it can cause an explosion to continue into areas where prior to the explosion only settled dust was present.

LITERATURE REVIEW

Experimental methods have established that if an atmosphere containing a cloud of dust of specified size and shape has an oxygen content in excess of 9% by volume (2) there exists minima for dust cloud concentration, ignition source temperature and emitted ignition source energy below which no explosion can occur. If all these minima are exceeded there can be an explosion.

The experimental data for dry sugar dusts summarised in Tables 1 and 2 have been reviewed elsewhere (3). Variation in the data measured are due to:

1. Differences in particle size, e.g., decreasing sugar dust particle size or increasing concentration lowers the minimum source temperature (9).

Table 1. --Minimum Values of Sugar Dust Explosion Variables

Ignition Source	Minimum Explosive Concentration g./m^3	Particle Size Microns	Ignition Source Temperature °C. in air	Minimum Ignition Energy Millijoules	Date and Reference Number
Hot wall tube	-	-	460		1911 (4)
Hot wire in flask	-	-	540-805		1915 (5)
Hot wire in flask	17	-	410		1922 (2)
Hot wall tube	10.3	-	650		1924 (6)
Bunsen Flame	66.0	-	-		1948 (7)
Electrostatic Spark in Flask	150	79		500-600	1950 (8)
Hot wall Flask	48	40-250	458-420		1952 (9)
Induction Spark in closed volume 18 in. x 14 in. diam.	40 120 180 320	44 62 71 81			1954 (10)
Induction Spark in closed volume 12 in. x 2-3/4 in. diam.					1961 (11)
Sucrose	45	less	420	100	
Refined sugar	35	than	370	30	
Raw sugar	45	80	350	40	
Not stated. Sugar Analysis Moist % Ash %					1967 (12)
0.083 0.019	13	less			
0.087 0.043	10	than			
0.078 0.025	8	70			

2. Differences in method of ignition, e.g., the proportion of total energy provided by the source that is radiant.
3. Differences in the rate of heating.
4. Differences in experimental technique centering on the production of reproducible uniform dust clouds.

The flame velocity in a sugar dust cloud of concentration 60 g./m^3 has been measured. It averaged 530 ft. per second but was found in the experimental apparatus to increase with the distance of travel to a maximum of 810 ft. per second (13). Schneider and Schliephake (14) showed theoretically that flame velocities in sugar dust clouds increase with decreasing particle size and increasing dust concentration to about 300 g./m^3.

The combustion wave may proceed through a dust cloud leaving behind some

Table 2. --Pressure Generation Caused by a Sugar Dust Explosion

Dust Particle size microns	Container size	Dust Cloud Concentration g./m^3	Maximum Pressure Recorded psi			Maximum Rate of Pressure rise psi/sec			Reference No.
			Sucrose	Refined Sugar	Raw Sugar	Sucrose	Refined Sugar	Raw Sugar	
less than 80	12 in. x 2-3/4 in. diam.	100	42	37	38	1600	1000	1100	11
		200	77	76	78	2100	4000	2300	
		500	142	91	132	2500	5000	1800	
		1000	152	109	154	1400	4700	1400	
		2000	-	93	-	-	2200	-	
40	18 in. x 14 in. diam.	240	76			195			10
120		280	71			160			
180		320	67			125			
320		450	57			95			
less than 70	Not stated	50		15					12
		100		30					
		150		45					

unburned dust and then flash through again when air is added to the system through vents, broken windows, etc. if the original ignition source or another adequate one persists. Thus there is some doubt as to whether in practice a maximum explosive concentration exists. However, in one sealed system a value for sugar dust has been measured to be 13,500 g./m^3 (2) which is 2.7 times the stoichiometric value for complete combustion in air.

The measurements of pressure generation and its rate of rise and peak value are difficult but have been made. The data are of limited value but can be used for the design of pressure release systems. Errors are introduced because the data depend on the volume of the experimental vessel (Table 2). However the data of Table 2 do indicate an optimum cloud concentration for maximum explosion severity.

In practice the knowledge of data on pressure is not considered important; any explosion should be avoided.

Little has been written about the formation and source of sugar dust. Geck (15) has commented on the production of dust in German refineries and concluded that though rotary driers, bucket elevators, slides and chutes all lead to dust, much more is formed in cylindrical sieves.

Andersson, et. al., (16) concluded that sugar dust occurs by chipping from the crystal surfaces and sometimes when agglomerates are broken apart. The amount generated consisted of a constant fraction related to the equipment used and a variable part influenced by variations in operation. An increase in conglomerates caused by bad vacuum pan operation or fugalling and an increase in sugar temperature increase dust generation.

The effect of moisture content on sugar dust generation has not been studied but could in part be responsible for dust generation in driers. The water content of sugar dust being dependent on atmospheric relative humidity sugar purity and to some degree

temperature can reduce the explosive hazard if it causes the air borne particles to become sticky and agglomerate. Explosions may be inhibited because the energy emitted from the ignition source is dissipated in evaporating the surface moisture. Also the moisture evaporated will increase the water vapour in the surrounding gas layer.

EXPERIMENTAL INVESTIGATIONS

During the present experimental study the air temperature was 70° F. (±2° F.), the pressure atmospheric and the relative humidity 40-60% i. e. below that required for the surface of the sugar to become sticky.

The sugar (500 g.) from which the dust was prepared was dried in a vacuum oven for 15 hours at 60° C., ball milled for 2 hours and then sieved in 100 g. lots. Various dust size fractions were collected, dried and resieved. These dusts were stored in desiccators over silica gel at room temperature. Only Australian sugars were used, their analyses being given in Table 3.

Table 3. --Analyses of Sugars, as Received, From Which Sugar Dusts were Made

	Brand 1	Brand 2	Brand 3
Cane Sugar	99. 92	98. 75	97. 38
Reducing Sugar	0. 011	0. 27	0. 59
Ash	0. 012	0. 30	0. 62
Other Organic Matter	0. 012	0. 4	0. 73
Moisture	0. 045	0. 29	0. 68

The dust dispersing device consisted of a 3 in. length of iron pipe closed at one end by metal gauze. The mesh of this gauze was one B. S. rating greater than that through which all the dust was just able to pass i. e. B. S. 100 mesh gauze for -120/+150 B. S. mesh dust. The container with the gauze facing downwards was separated from an electromagnet by a soft rubber sponge; the applied voltage determined the amplitude of the vibration achieved and thus determined the rate at which sugar dust fell through the gauze. It was found that the dust flow rate was reproducible only if the container was filled to a depth greater than 1-1/2 in. The flow rate of the dust could also be varied by using different diameter containers. Only dry sugar dusts were used because moist dusts could not be adequately dispersed using the device.

With the device situated at the top of a vertical glass tube, dust concentration profiles were measured using a sampling probe made from 10 glass tubes (5 mm. diameter) cemented along a rod. The best profiles were achieved when the dust container base was 1/2 in. above the tube top end and 4 circular brass B. S. 16 gauzes were inserted 1, 2, 4, and 10 in. respectively from the flame tube top.

The cloud was uniform after passing the second mesh i. e. through 86. 5% of the tube's volume.

The minimum explosive concentration (MEC) was determined for a fixed size and type of sugar dust by varying the rate of feed and attempting to ignite the cloud with a town gas flame. At the MEC the flame propagated through the cloud in the tube to be arrested at the lowest gauze.

When flame propagation occurred the dust and town gas supplies were stopped. The flame tube was removed, washed, dried and reinstalled. The dust supply was then recommenced and the flow rate determined. Normally this was done by weighing the dust collected on a glass dish at the lower end of the tube over a given time (g. /sec). Dusts of less than 100 microns were collected on a facial tissue folded into a funnel shape so as to cover the entrance of a 3 in. diameter glass tube that was connected to a vacuum tap. With the vacuum adjusted so that the tissue was just held on the tube, this tube was held beneath the flame tube and the dust collected in a measured time weighed.

The rate of descent of the dust through the tube was measured by two operators who

timed the passage of the interface of discrete dust clouds caused by stopping and starting the vibrator. The average of 20 measurements was recorded, the error being ±5%.

As the volume of the flame tube was known the concentration of the sugar dust in the tube could be obtained when flame propagation was achieved:-

$$\text{MEC} = \frac{\text{dust mass flow rate g./sec.}}{\text{tube volume } (m^3)} \times \text{time of fall sec. } \pm 5\% \times \frac{1}{\text{tube volume } (m^3)} = \text{g./m}^3 \pm 19\%$$

As the error in the measurement due to variations in the dust concentration was estimated, glass flame tubes of differing diameters were used to assess the error for heat transfer differences from the ignition source to the dust cloud using the same experimental technique and precautions.

The results obtained, shown in Fig. 1 for Brand 1 sugar dust, indicate that higher heat losses increase the MEC. The determination of the MEC will be subject only to the errors of cloud dispersion if the flame tube diameter is greater than 3 in.

The results shown in Fig. 2 were determined for a 3 in. diameter flame tube 15 in. long.

To conclude from these results that Brand 1 sugar dust has a lower MEC than Brand 2 which has a lower MEC than Brand 3, for a sugar dust particle size range of say 152-211 microns would involve the assumptions:-

(a) the dust samples used had the same particle size distribution, and
(b) the dust cloud produced was exactly the same.

The error in assumption (b) would be less than the average increases in the MEC of the dusts.

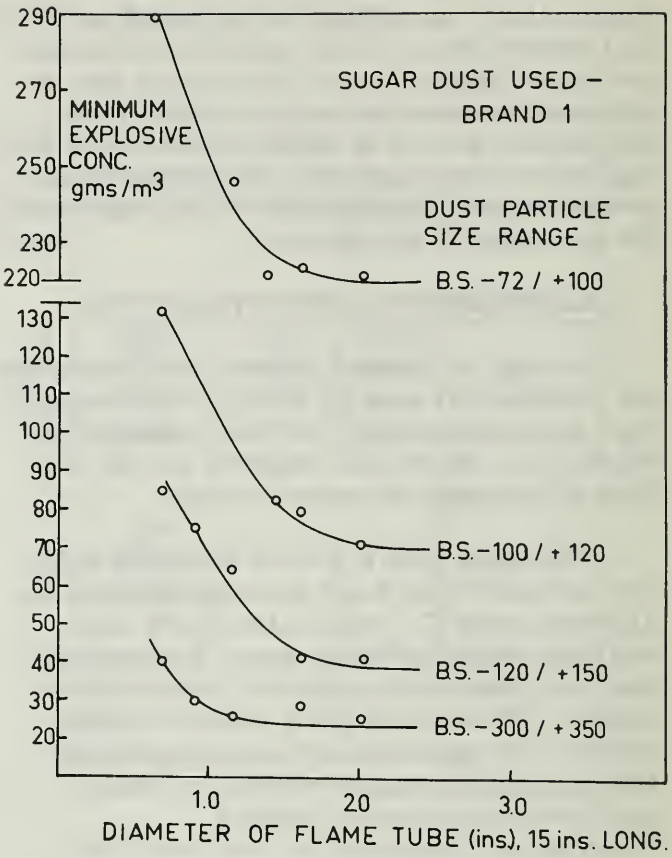

Figure 1. Effect of tube diameter on evaluation of minimum explosive concentration of sugar dust.

The Quenching Distance. During the experiments to determine the effect of heat transfer on the MEC it was found that for a given dust particle size a certain diameter tube exists for which the flame will not propagate up the tube. The results of the minima obtained for copper and glass flame tubes are shown in Fig. 3. For instance, for Brand 1 sugar dust of 100/+120 B. S. (particle size 125-152 microns) shown by A. B. on Fig. 3 the minimum diameter glass tube for flame propagation was 0. 45 in. and for copper 0. 9 in. Such an observation could be explained by the heat transfer or possibly the free radical mechanism of flame propagation for gas-air explosive mixtures proposed by others (17).

An interesting concept that emerges from the data of Fig. 3 is that there exists a

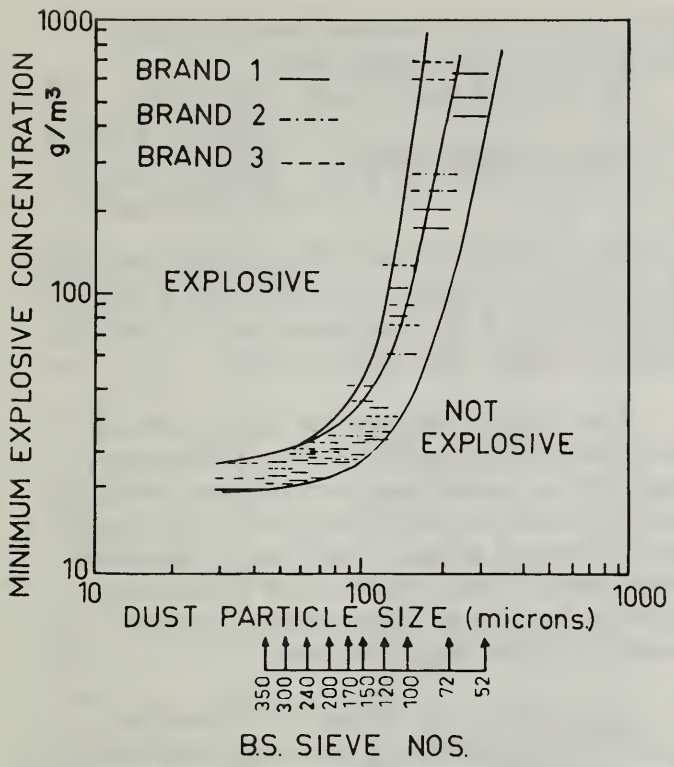

Figure 2. Effect of dust particle size on minimum explosive concentration.

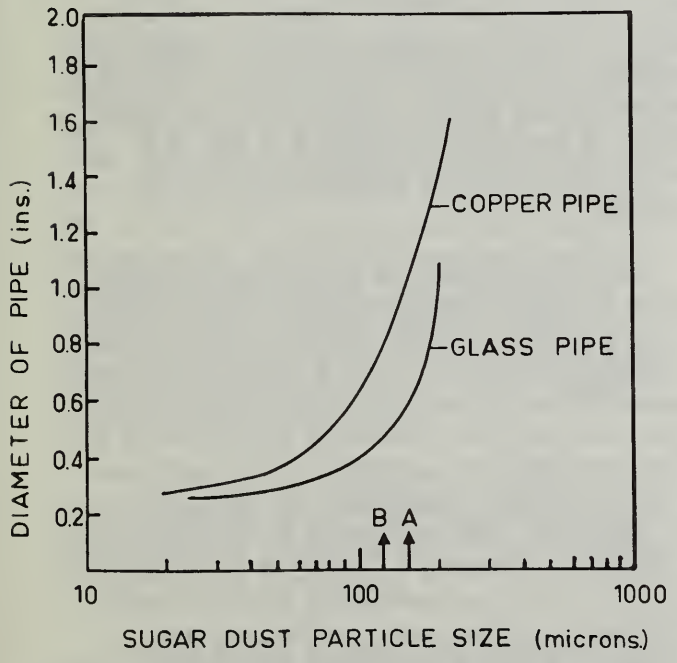

Figure 3. Minimum size of tubes for flame propagation.

minimum cloud volume for flame propagation. Since a dust cloud requires a certain amount of energy to cause flame propagation, this minimum energy for ignition must ignite a minimum volume of dust.

Examination of Fig. 3 shows that as the sugar dust particle size decreases the diameter of the minimum cloud volume becomes independent of the flame tube material and approaches the value of 0.25 in. It is suggested that this dimension is the true quenching distance; that is, the minimum aperture between inert solids through which a flame will propagate. It has already been shown that a sugar flame will not propagate past a No. 16 B.S. gauze.

The Minimum Ignition Energy (MIE). The MIE required for flame propagation in a sugar dust cloud at the MEC was measured by two techniques. The first used the apparatus described earlier and determined the MIE directly from the calorific value and volumetric rate of town gas burned, that was just sufficient to ignite the cloud.

The second method allowed the dust to fall through a pipe heated uniformly by induction. The pipe wall temperature was increased incrementally until ignition occurred. The pipe temperature was then reduced just below the critical value and the average temperature of the dust which emerged from the tube was measured with a thermometer. A heat balance determined the energy input to the dust cloud.

At ignition the pipe wall temperature, measured with a thermocouple was always within the range 380-410° C. This is reasonably close to the data on sugar dust cloud ignition temperatures recorded in Table 1.

Thus the first method tended to overestimate and the second method tended to underestimate the MIE. The heat input was expressed as millijoules required to cause flame propagation in a cloud at the MEC.

The results obtained by the two methods are shown in Fig. 4 which are average values for Brands 1, 2, 3 dusts.

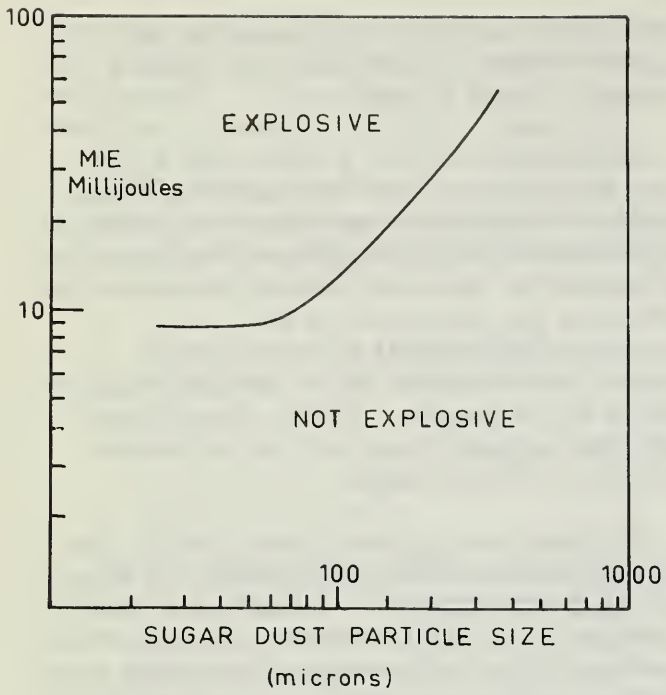

Figure 4. Minimum ignition energy for sugar dust explosions.

Industrial Dusts. Samples of sugar dust were collected from a refinery sugar silo and from a bulk sugar terminal. The analyses are shown in Table 4.

Table 4.

	Moisture Content %	Pol.	Ash
Refined Sugar	0.04	99.95 Approx.	0.01 Approx.
Refined Sugar Dust	0.12	99.25	0.24
Raw Sugar	0.5 Approx.	98.0 Approx.	0.3 Approx.
Raw Sugar Dust	0.32	95.01	0.26

The dusts were dried and on sieving passed a 300 B.S. sieve indicating that the particle size was less than 50 microns.

The results of the measurements of MEC and MIE for these dusts were:

(a) Refined sugar dust - MEC 200 g./m^3
MIE 18.0, mj

(b) Raw sugar dust - MEC 150 g./m^3
MIE 18.0, mj

From Figure 2 the MEC for similar pure dusts would be expected to be about 25 g./m^3. From Figure 4 the minimum ignition energy expected would have been 7 mj.

Dust falling through the flame tube at the minimum explosive concentration was collected on a microscope slide and the photographs taken compared with those of laboratory prepared dusts. The comparison indicated that at least some of the differences between factory and laboratory samples could be due to agglomeration.

Discussion. If radiant heat transfer controls the process of heat exchange between the ignition source and the dust cloud, the number of particles/unit volume at the MEC will be relatively independent of their size. Column 4 of Table 5 partly confirms this, the average number of cubic sugar dust particles/in^3 being equal to 7450. Column 5 shows that the surface area/unit dust cloud volume is almost independent of the dust particle size below a particle size of 97 microns.

Since the number of particles/unit volume in a sugar dust cloud at the MEC does not vary greatly then if the distance between the dust particles exceeds a critical distance flame will not propagate. The critical distance of separation should be comparable to twice the radius of a sphere of air sufficient for the complete combustion of the sugar dust particle. The distances of separation are shown in Column 6, Table 5 calculated from the MEC data assuming that the dust particles in a cloud are in cubic array. Column 7, Table 5 shows the spherical air envelope radius calculated as one half this distance of separation. Column 8 of Table 5 shows the spherical air envelope radii calculated from the stoichiometric

Table 5.

1 Particle Size Fraction B. S. Mesh	2 Average Dust Particle Size Microns	3 Average M. E. C. g. /m^3	4 Number of particles per m^3 x 10^{-6}	5 Dust Cloud Surface Area cm^2/cm^3 x 10^{-4}	6 Distance apart of Particles	7 Radius of air envelope cm.	8 Calculated Radius of air envelope cm. at different temperatures		
							25° C	300° C	450° C
-52/+72	253	539	211	8.08	0.337	0.168	0.231	0.293	0.315
-72/+100	182	363	383	7.62	0.279	0.14	0.166	0.211	0.226
-100/ +120	139	85	200	2.3	0.347	0.173	0.127	0.161	0.173
-120/ +150	115	35	146	1.15	0.399	0.199	0.105	0.133	0.143
-150/ +170	97	36	246	1.41	0.334	0.167	0.089	0.113	0.121
-170/ +200	83	28	310	1.28	0.31	0.155	0.076	0.096	0.103
-200/ +240	69	26	502	1.42	0.264	0.132	0.063	0.079	0.085
-240/ +300	58	25	811	1.63	0.225	0.113	0.053	0.067	0.072
-300/ +350	49	24	1285	1.83	0.193	0.096	0.043	0.058	0.061

equation for complete combustion as a function of air temperature. Comparison of the figures given in Columns 7 and 8, Table 5 show an order of agreement of about 2,i. e. the distance apart of the dust particles at the MEC is about four times the radius of the spherical air envelope necessary for complete combustion. The agreement between these figures appears better as the air temperature increases, suggesting that the flame heats the air, and as the particle size decreases.

It is also interesting to compare the distance apart of the dust particles at the MEC with the proposed quenching distance of 0. 25 in. or 0. 63 cm.

Again as the number of particles/unit volume in a sugar dust cloud at the MEC is approximately constant, light scattering techniques may be well adapted to measure sugar dust concentration in industrial atmospheres.

Comparison of the factory and laboratory dust analyses supports the crystal surface attrition mechanism for dust generation suggested by Andersson et. al. (16). If most of the impurities associated with a sugar crystal are at or near the surface then dust samples taken from the first stage of crystal transport will have a somewhat lower purity than those taken later in the process. Thus MEC may be anticipated to decrease at least slightly with an increase in the length of crystal transport. Thus the distribution of impurities through the crystal govern the MEC and MIE of the dust generated. This assumes that there would be no change in agglomeration which is probably often not true and also ignores differences in crystal transport systems.

CONCLUSIONS

Experimental determinations showed that the minimum explosive concentration (MEC) and the minimum ignition energy

(MIE) of dry sugar dust increased with an increase in dust particle size. For sugar dusts prepared by ball milling samples of Australian sugars the measurements showed that below a dust particle size of 100 microns the MEC and MIE were constant at 20 g./cubic metre and 10 millijoules respectively. At the MEC the number of dust particles per unit volume was shown to be approximately constant at 5×10^8 particles/cubic metre.

Measurements of the MEC and MIE of dry industrial sugar dusts have suggested that factors other than dust particle size affect experimental determinations of these explosion variables.

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DISCUSSION

H. J. Reiche (Refined Syrups): Dr. Edwards, how would you go about measuring the dust concentration of the sugar dust atmosphere in the refinery?

R. E. Edwards (Colonial, Australia): We have, in fact, measured some of these dusty atmospheres in our refineries, and they have been quite low - of the order of 0.2 gram per cubic meter. The method is quite simple: a known volume of air is sucked from the atmosphere through a tube, the other tube end being immersed in water, the total solids in the water are then determined. There are more sophisticated methods than this one but I prefer it because it gives a direct measurement, and some of the others - the electronic ones - need calibration.

C. W. Beal (C&H): We refine in this Bay area where the humidity is generally high. What are your thoughts about humidity in general?

R. E. Edwards: I think humidity will help you because it tends to promote agglomera-

tion of the dust in the air. The NFPA statistics on explosions show that more sugar dust explosions occur in the winter than in the summer. As winter is the time of low humidity, the statistics also show the higher the humidity the less the risk.

C. W. Davis (Colonial, Australia): I wonder if you could describe to the people what your minimum concentration of 20 grams per cubic meter looks like.

R. E. Edwards: A dust concentration of 20 grams per cubic meter is rather like a very hard rain. If you stand in an atmosphere of 20 grams per cubic meter, you can see approximately 8 to 10 feet.

A. Clarno (Savannah): Where do you consider the most dangerous place for explosions in a refinery. In a silo, where sugar is falling, say 50 feet? In elevators, or in conveyor belts that are running in tunnels which have static charges on them? Where does your company consider the most likely place for this condition to develop?

R. E. Edwards: Our feeling is that, wherever you start to move crystals, whether it be by bucket elevators, in the silo, or any place, that's a hazardous area. I feel that no area is more hazardous than another. A long time ago, C. S. R. used to operate the silos and bucket elevators in groups by just allowing the bucket elevator to churn when the silo was full, and I understand that in there you couldn't see the end of your nose, let alone your hand in front of your face. But we don't do this any more. But, if you have this condition a bolt could shear as the buckets are forced through the sugar, and that's a risk that should be eliminated. Wherever you transport granulated refined sugar, I think dust will be there, and it's best to try and measure dust concentrations in as many areas as you possibly can. It is a good precaution.

A. Clarno: Is it still true that in sugar falling 50 or 60 feet from the point of discharge into a silo, Stokes' law of sedimentation will cause static charges to develop?

R. E. Edwards: That's a difficult question and really I cannot give you an answer. But I can comment. Static charge is something which really nobody knows much about, although Eric Cuneen and I had a look at it. All we were able to say to ourselves was that we don't know much about it either, nor were we able to say that a particular mechanism for static generation is correct. One of the things about sugar discharge into a silo is that you tend to get a compression of the dusty atmosphere towards the end of silo filling. When you start off, the silo is, say, empty, and you have a dilute dusty atmosphere, but when you are near the silo top, there is a high concentration of that fine dust which obeys Stokes' Law and doesn't settle very quickly. What I'm suggesting here is perhaps the existence of an optimum hazard condition. I think that the problem solution is dust concentration measurement.

K. Schoenrock (Amalgamated): Do I understand you correctly then, that you always need a spark to start the explosion?

R. E. Edwards: You need a spark, electrical, electrostatic, or mechanical, or a hot bearing, or any source which is above, say, 380° C. and which can give out more than 9 millijoules and generally a spark is above this.

K. Schoenrock: The magical number apparently is 20 grams per cubic meter. Under these concentrations you have not obtained any explosions. If you had some freak conditions, could an explosion occur under 20 grams per cubic meter?

R. E. Edwards: I would say no, and would add that I think dust explosions are transient phenomena. You can go into the refinery five days a week and you will never measure a concentration of this order - 20 grams per cubic meter - in fact if it gets to 10 I think it dangerous. But, statistically, sugar dust explosions average about 1-1/2 per year - I don't know how you can have half an explosion, but this average could mean that you get your transient condition once every 8

months (multiplied by the number of Sugar Refineries for which the above average figure was derived). In my experiments I didn't get flames to propagate through clouds that were below 20 grams per cubic meter. But in the refinery it's better to work at a much safer, that is, a lower level, obviously because you do not know what sort of transient conditions are possible and you must correct for that. I wouldn't like to be in an atmosphere in a refinery at 20 grams per cubic meter.

F. Bruder (SuCrest): You mentioned that the concentration is important. In no area is dust more concentrated than in dust collectors. Now, you want to keep the dust content down, and yet you want to collect the dust. What have you people done about dust collecting?

R. E. Edwards: The dust collecting systems that we use are rotaclones; we have very large ducts on high air velocities and I would suggest to you that a 20 gram per cubic meter condition would be rare. However, the samples of dusts from refineries that I tested did have high ash contents and correspondingly higher minimum explosive concentrations.

A material balance on the spray water used in the rotaclone would give you a quick check on dust concentrations in the dust collection system. I did see some figures for this for one of our refinery's rotaclones and although I cannot remember the exact figures, the above sugar mass balance calculation showed the dust concentration much lower than 20 grams per cubic meter.

FOURTH SESSION: Symposium on Raw Sugar Quality Standards

E. J. Culp, American Sugar Co., New York, Moderator

W. R. Tuson (Colonial, USA): The refining quality of raw sugars is not a new subject, it is one that has been bandied about for years. It is only within the past year or two, however, that such discussions were possible against a frame of reference and all of us should feel indebted to our moderator, Jim Culp, and his associates for providing such a frame of reference through their work in establishing their Company's standards for raw sugar purchase. We, at Colonial, take exception to some of these standards because evaluation of a raw material must be based on the particular plant or refinery in which the raw sugar is used and hence is a very subjective question. None of our refineries have the same strength or weaknesses, in fact in many cases we do not even have the same refining processes. It is obvious that ten or twelve different sets of standards, one for each Company here represented, would be completely impractical for the raw sugar producers and completely defeat the primary purpose of such standards, viz., to assure improvement in quality of substandard raws. It is sincerely to be hoped that open discussion such as we have here will ultimately result in objective standards that will have meaning and value for all refiners.

We, at Colonial, have been evaluating raw sugars on a formal basis for about twenty years. Originally begun, to serve as a guide for our own Company's mills in Cuba which supplied seventy-five percent of our meltings, each cargo was evaluated in detail for each refinery station, this in addition to the regular analytical tests normally performed on raw sugars. With the loss of our Cuban mills, the evaluation was continued to serve as a guide to our Raw Sugar Purchasing Department with respect to desirable countries and Ports of Origin. With the advent of the American Sugar Company's raw sugar standards, we, at the refinery, were asked to express our judgment as to their applicability insofar as our Company's operations were concerned. To arrive at an opinion we made a statistical analysis of all our analytical and performance data covering a total of 28 distinct

areas of origin representing over two billion pounds of raw sugar. Some of the resulting observations will be presented here.

Our first comment is an obvious one. Since we employ phosphoric acid and frothing clarifiers, filterability has no meaning for us at all. We feel, however, that the insolubles test provides a good criterion of performance of one extremely important raw mill operation, one which markedly effects the quality of their product, viz., clarification. An insolubles test is a relatively simple one and should have a good correlation between filterability and scums production. I suspect that Jim Culp found no such correlation otherwise he would not have gone to the more complicated and less replicable filterability test. We have found a general correlation between insolubles and overall refining quality, but no specific relationship with scums production. We suspect that this is because we are lumping all insolubles, coarse, fine and semi-colloidal, together. It should be relatively simple to modify the insolubles test procedure in such fashion, that we would measure the insolubles in two or three segments. In such a manner we might find good correlation between such a test and filterability on the one hand and scums production on the other hand which would be a meaningful step forward.

We would next like to take up the question of Ash-Non Sucrose Solids (NSS) ratio which has been one of the more controversial points in the American's specifications. It resulted in a brief for the defense of the raw sugar industry, which won the "Meade prize for the best paper" at S. I. T.'s annual meeting in 1967. We have no desire to beat a dead horse or even a live one for that matter but we have certain comments and suggestions which we feel have validity. The Ash/NSS is supposed to provide a measure of a raw sugar's pan scaling and molasses forming properties. We must state that we have been unable to find a relationship between Ash/NSS and final molasses production by any of the indicators which we apply to judge this area of refinery performance. To be honest, we found this most surprising, because, off the top of our heads, we would have thought the relationship would have existed. We could not find it, however.

Pan scaling is important because of reduced heat transfer and extended boiling times, but even more critical in these times is the necessity to exclude such pan scale if formed from the final granulated sugar produced. This has, on occasion, with extremely bad pan scaling raws, required boiling white pans out to remove scale on a 48 or 72 hour cycle notwithstanding the attendant serious loss of production and increased cost.

To discuss this phase I would like to refer to Table 1 which provides our complete analysis and total receipts of raws from five different origins, as well as our refining experience with the same. I would like to point out that we could have selected any other origins and come up with the same conclusions, as the comments about to be expressed have been completely supported by our statistical analysis, which, as I mentioned before, covered 28 separate origins and one million tons of raws.

In Table 1, origin F shows the weighted average of all of the cargoes from this origin, all of which had Ash/NSS in excess of American's standards. You will note that they were bad pan scalers; in fact the worst we have received in this respect. If you will now look at the column headed origin C which is divided into subcolumns C_1 & C_2. This represents all the raws received from Origin C divided on the basis of those that meet Ash/NSS and those that did not. The only difference between C_1 and C_2 raws was the Ash/NSS. They were equally bad with respect to pan scaling and only slightly better than origin F which is saying nothing in their favor.

If we now look at origin E you will note that although both subdivisions fall within American's limits of Ash/NSS one subdivision gave no pan scaling at all while the

Table 1

	Origin F	Origin C		Origin E		Origin D		Origin P
		C_1	C_2	E_1	E_2	D_1	D_2	
Quantity (Tons)	19,700	40,500	39,600	5,500	63,900	46,000	29,000	12,800
POL	97.74	98.06	98.14	97.90	97.42	98.67	98.75	97.92
% H_2O	0.31	0.31	0.37	0.26	0.42	0.27	0.27	0.45
% R.S.	0.40	0.45	0.28	0.60	0.64	0.31	0.25	0.51
% ASH	0.77	0.41	0.56	0.43	0.49	0.29	0.38	0.44
% ORG.	0.78	0.77	0.65	0.81	1.03	0.46	0.35	0.68
ppm SO_4 Raw	1598	1244	1539	460	1020	483	656	1068
ppm SO_4 W.S.	1247	730	908	153	628	300	110	249
Pan Scale	Bad	Bad	Bad	Neg	Poor	Neg	Neg	Neg
Decolorization	Poor	Poor	Poor	Fair	Poor	Good	Good	Good
Overall Rating	Bad	Poor	Poor	Fair	Bad	Exc.	Exc.	Exc.
Ash/NSS	0.39	0.25	0.38	0.23	0.23	0.27	0.39	0.27

other was most unsatisfactory in this respect, although not as bad as the two prior origins mentioned.

Moving to origin D you will note that once again we have subdivisions representing those raws which meet and fail to meet the Ash/NSS. In this case, however, no pan scaling was experienced with either raw class.

We feel it is conclusive from this data that Ash/NSS has no bearing on pan scaling. We could substantiate this with other origins and examples but feel that in the interests of brevity the above sample of 260,000 tons of raws is indicative.

You will note, however, that in all cases where pan scaling has been high, the SO_4 Anion measured on the raw sugar has been high regardless of Ash/NSS. Note origin C, Ash/NSS 0.25, SO_4 in raw 1244 ppm or origin E_2 where Ash/NSS is 0.23 but SO_4 in raw is 1020 ppm. Of course when Ash/NSS has been high, SO_4 values have been even worse: 1598 ppm, 1539 ppm respectively. On the other hand where pan scaling has been negligible we see SO_4 values of 460, 483, and 656 ppm on the raw, regardless of Ash/NSS.

Perhaps we should now look at origin P with a normal Ash/NSS but a high SO_4 in the raw. You will note that here pan scaling was negligible. However, SO_4 in the washed sugar was only 249 ppm, a rather unusual feature since most raws with high SO_4 yield a washed sugar high in SO_4. This origin P, by the way, is the only one of 28 which does not follow the pattern of high SO_4 values in raw, and high SO_4 values in washed sugar.

We would therefore conclude from Table 1 that high SO_4 values in the washed sugar will produce serious pan scaling. As a practical limit our experience would indicate a value of 400 ppm as the dividing line between acceptable and unacceptable pan scalers.

It is an interesting corollary to pan scaling that in our experience the level of 400 ppm in the washed sugar is an approximate dividing point between washed sugars which decolorize well and those that do not. By this I do not mean that at 399 ppm everything is fine and that at 401 ppm the roof falls in, but that in this range you get a markedly decreased effectiveness in bone char's ability to remove color, and an even more marked decrease in effectiveness of decolorizing resins ability to remove color, which becomes

progressively worse with increasing SO_4 values. This of course immediately brings to mind and confirms the Carpenter, Larry, Deitz Excess Polyvalent Anion Theory (1) mentioned in proceedings of this organization's predecessor, the Bone Char Research Project.

While on the subject of color, we have found little if any correlation between raw sugar color and pan liquor and granulated sugar color. Some high color value raws produce excellent pan liquor and sugar, others do not, while some low color raws produce poor pan liquor and sugar, others do not. Even working with washed sugar colors the degree of consistency is not satisfactory. In this evaluation we are excluding those raws where high SO_4 values in the washed sugar adversely affects color removal as mentioned above. It could be theorized from the foregoing that in tailoring our color measurement techniques to the predominant colorants present in raw sugars, sufficient weight is not given to those colorants less readily eliminated by the refining techniques we employ, as we have heard in previous papers at this Technical Session.

Probably the most important characteristic of any raw is its affinability. American's standards measure this by determining the quantity of sugar of finer granulation than an arbitrary standard of fineness. Other technologists have suggested that uniformity of crystal size regardless of fineness would be a better criterion of expected performance. No matter which you choose, however, three major factors in a raw sugar's affinability are ignored, viz., degree of conglomerates, quantity of impurities occluded in the crystal and viscosity of the residual syrup on the raw sugar crystal.

(1) Carpenter, F. G., Larry, D., and Deitz, V. R., Proc. Seventh Tech. Sess. Bone Char 1961 p. 259 (1962); Bone Char Tech. Report No. 69 (1962).

Referring to Table 2, we show the two worst cargoes of raws processed by our refinery. Both of these raws would be acceptable as far as grain size is concerned. The bad refining character of these two cargoes, however, was due to their poor affinability. We set our Wash Plant centrifugal cycles to provide a washed sugar with less than 0.1% RS (reducing sugars). Looking at Column 1, you will note that at a 180-8 cycle, which is 180 seconds total cycle with 8 seconds of water and 53 seconds drying time after final water application, RS was 0.17% and ash 0.23%. An increase of 1 second or 12-1/2% in water quantity and an additional 9 seconds drying time did practically nothing to improve washed sugar quality. This is a classic example of occluded impurities.

Table 2.

Quantity (Tons)	13,000	5,800
POL	97.20	95.65
% H_2O	0.54	0.91
% RS	0.85	1.45
% Ash	0.44	0.53
% Org.	0.97	1.46
Ash/NSS	0.19	0.15
W.S. (180-8) % RS	0.17	0.22
W.S. (180-8) % Ash	0.23	0.14
W.S. (190-9) % RS	0.16	0.12
W.S. (190-9) % Ash	0.23	0.09
*W.S. (190-9) % RS		0.23
*W.S. (190-9) % Ash		0.13

*After 5 hours operation

In the second case, column two, close to an acceptable washed sugar was produced at the extended cycle of 190-9 which includes 62 seconds drying time, but after five hours operation at this cycle washed sugar quality had retrogressed to values obtained with shorter cycles and less water, and was of completely unacceptable quality. Further, at this point no cycle variations or magma temperature variations could return quality to even close to acceptable values. Investiga-

tion disclosed that initial mingling was with affination from the prior raw being melted having a viscosity of 400 cp. After four hours, we estimate that about 3-1/2 hours would be required to replace all the former affination, affination syrup viscosity peaked at 1100 cp. The only practical method of working off this raw was to refine this material for three hour periods in each twelve to sixteen operating hours. The other alternative, to mingle with water and remove produced affination as formed, was completely impractical.

The two examples above, while unique in their severity, were typical of other cargoes which exhibited the same characteristics even though to a lesser degree.

In summary, we have found very poor correlation between tests applied directly to a raw sugar and its refining quality, with the exception of measurement of the sulfate anion. That development of a standard affination procedure, taking into account the viscosity of the syrup adherent to the raw, with appropriate testing of the washed sugar so obtained, would provide a more meaningful evaluation of the refining qualities of a raw sugar.

Joseph A. Harrison (Supreme): Being from Supreme Sugar, I speak with a slightly different point of view than my fellow panelists in that we, in addition to being a refiner, are also a processor of raw sugar.

During the harvest season in Louisiana, we grind approximately 4,000 tons of cane per day and process the raws produced from this cane directly into refined sugar, so we are aware of the many problems that the processor of raws has.

In addition to the raws we produce during grinding, we purchase the entire output of raws from five other mills in Louisiana.

We receive these raws during the grinding season which is three months, and during the next four months.

Our total raw receipts for the year approximate 50% offshore and 50% Louisiana Sugars.

Normally Louisiana raw sugar is of excellent quality, but due to many reasons, such as high labor turnover, economic pressures, hurricanes, and early freezes, we noted a slow but obvious falling off of this quality during the 60's that reached its lowest point in the 1965 crop.

At the conclusion of the 1965 grinding season we met with the representatives of these five mills, and in the course of discussions with them, agreed that there would be and should be a set of Standards acceptable to both sides; so, contrary to most opinions, we were the first to apply a set of Standards and Penalties in the buying of raw sugar, but it was limited to our purchases from mills within the State of Louisiana. I might also add that we neglected to include premiums.

I would like to say at this point that the majority of Louisiana mills are privately held family organizations, or cooperatives, who have a deep sense of pride in their product and our discussions with them were amicable and without any major hurdles. As a result of these discussions it was agreed that all sugar purchased by Supreme from Louisiana mills in 1966 would be purchased under the following set of Standards and Penalties (page 143).

Before we established these standards and penalties we had done much investigation of our own on Louisiana raw sugars, and again, pertinent to what Bob Tuson has said, our processing is completely different from his, so our problems were completely different.

Our contract further stated that if any of the specifications got above the maximum in the table, that is above the 2% penalty, then these sugars were rejectable and subject to negotiation.

STANDARDS AND PENALTIES

TEMPERATURE, INVERT, AND GRAIN SIZE

STANDARDS: Temperature - 100° F. or less
Invert - 0.0% - 1.00%
Grain Size - 0.0% - 4.9% through 35 mesh Tyler Standard Screen

PENALTIES:

Temperature		Invert		Grain Size	
Degrees F.	Deduction %	Test %	Deduction %	Screening (A)	Deduction %
101	.03	1.01 - 1.03	.03	5.0 - 5.4	.05
102	.06	1.04 - 1.06	.07	5.5 - 5.9	.10
103	.09	1.07 - 1.08	.10	6.0 - 6.4	.15
104	.12	1.09 - 1.11	.13	6.5 - 6.9	.20
105	.15	1.12 - 1.14	.17	7.0 - 7.4	.25
106	.18	1.15 - 1.17	.20	7.5 - 7.9	.30
107	.21	1.18 - 1.19	.23	8.0 - 8.4	.35
108	.24	1.20 - 1.22	.27	8.5 - 8.9	.40
109	.27	1.23 - 1.25	.30	9.0 - 9.4	.45
110	.30	1.26 - 1.28	.36	9.5 - 9.9	.50
111	.36	1.29 - 1.30	.43	10.0 - 10.4	.65
112	.43	1.31 - 1.33	.50	10.5 - 10.9	.80
113	.50	1.34 - 1.36	.57	11.0 - 11.4	.95
114	.57	1.37 - 1.39	.64	11.5 - 11.9	1.10
115	.64	1.40 - 1.41	.76	12.0 - 12.4	1.25
116	.81	1.42 - 1.44	.89	12.5 - 12.9	1.40
117	.98	1.45 - 1.47	1.02	13.0 - 13.4	1.55
118	1.15	1.48 - 1.50	1.15	13.5 - 13.9	1.70
119	1.57	1.51 - 1.52	1.57	14.0 - 14.4	1.85
120	2.00	1.53 - 1.55	2.00	14.5 - 14.9	2.00

A. Represents % through 35 mesh Tyler Standard Screen

You will note that we used only three areas to be subject to these Standards and Penalties, because it was our opinion that if these Standards were met that the other areas would be acceptable, with one exception, ash. We did not include ash in these Standards because it was not a problem in raw sugars produced from Louisiana cane.

It may seem strange to include temperature in a set of Standards because this is not a normal problem when receiving offshore sugars, but due to close proximity of the Louisiana mills supplying us, it was a serious problem. We found that raws that were stored in the warehouse with temperatures in excess of 100° F deteriorated rapidly and the color pick up doubled in two months.

After the first week of the 1966 grinding season, we were pleasantly surprised, as were the mill owners, at the quality of the raw sugar delivered to us from these mills and from then until the end of the 1966 campaign there were very few deliveries outside of these Standards.

Being aware of the coming of the #10 Contract, we decided to abandon our Standards and apply the #10 Contract to our 1967 purchases of Louisiana raws which was agreeable to our suppliers. We purchased the

necessary equipment to run test under the #10 Contract and ran several tests on the 1966 crop of Louisiana raws and found that a goodly portion of this sugar would have been in the premium range.

As the 1967 Louisiana grinding season began and we started receiving raws from our various suppliers, we applied the Quality Standards Test of the #10 Contract except that we excluded the filterability test and continued to apply the temperature Standards as set forth in our above stated Standards.

Our experience on these sugars was that at the beginning of the grinding season most sugars received from these Louisiana suppliers were in the premium range in the area of ash, color, and grain size, but as the season progressed the sugars met the specifications of Standards without premium or penalty. This caused us to wonder if this trend were true also of offshore sugars, and so we went back in our records and checked the test we had run on offshore sugars of 1966, and compared these tests with the sugars purchased from the same countries under the #10 Contract during 1967 and 1968. The results of these comparisons indicated that six of the eight countries that we checked in 1966 would have received more premiums than penalties for their sugars delivered to us, but in 1967 these same countries were meeting the specifications or were slipping into the penalty range with very few premiums. In 1968 this trend has become even more obvious.

There certainly is no question in our mind, or I am sure, in the minds of other refiners that a set of Quality Standards relating to the purchase of raw sugar was desirable, and in fact necessary, but it is a question of whether the initiation of these Quality Standards has in fact achieved the supposed results.

We are all aware of the fear that struck the heart of the raw sugar producer when the question of Quality Standards with penalties and premiums was first mentioned; I know I was acutely aware of this feeling when I first had discussions with our Louisiana suppliers, but we now have two years experience with it and perhaps the feeling of suspicion of the refiner by the processor has moderated somewhat in that time.

I think Mr. Guillermo Aleman in his article "Facing the Quality Standard for Raw Sugar" in The Sugar Journal, May 1968, issue, sets forth the processor's advantages of complying with the Standards far better than I could.

In conclusion I would say that as a refiner, we are quite satisfied to buy our sugar under a set of Quality Standards; we, of course, would like to change some of these Standards to meet our individual refinery problems, but we recognize that other refiners have different problems with different parts of these Standards than we and, therefore, suggest no change.

We certainly have no quarrel with the testing procedures for the various Standards as set forth in these specifications except possibly the highly controversial filterability test.

Being a refiner, we are in the sugar business, not in the penalty or premium business, and would like to see all raws meet these Standards or we think the penalties and premiums should be changed to more accurately reflect the true cost incurred in processing penalty range sugar, or the savings realized in processing premium range sugar.

P. Petri (Godchaux-Henderson): The form that we use for the evaluation of raw sugars is shown on page 145.

This is a modification of the old Godchaux-Henderson form and is built around the No. 10 contract standards. However, we feel it necessary to add three additional criteria. For the affined sugar, in addition to grain size, filterability, and color, we also measure ash to arrive at a measure of the occluded ash in the sugar crystal. The percent ash removal in affination is an indi-

RAW SUGAR QUALITY EVALUATION

Seller _____ Vessel _____

Date unloaded _____ Country of origin _____

Tons received _____

Penalty/premium		Analysis	Quality range Max	Min
_____	Polarization	_____		97.3
	Sucrose	_____		
	Invert	_____	0.75	
_____	Ash	_____	.32xnon-suc	.16xnon-suc
	Moisture	_____	0.75	
	Organic non sugars	_____	0.80	
	Invert/ash	_____		
	Organic/ash	_____		
	Safety factor	_____	0.30	
_____	Color, ICUMSA	_____	230	100
_____	C&H	_____		
	pH	_____		
_____	Crystal size, -30 mesh US	_____	55	20
	Starch	_____		
	Sediment	_____		
_____	Filterability	_____	140	45
	Ash, affinated raw	_____		
	& removal	_____		

cation of wash plant effectiveness. An acceptable level of ash in the washed sugar is about .09%, or the equivalent of 80% removal. In cases of occluded ash, the removal will only be on the order of 60%. Therefore, we feel that the percent ash in the whole raw sugar does not tell the whole story. Also, as a guide for additional evaluation of quality, we have added Invert/Ash and Organic/Ash ratios. Criteria of good raws are ratios of 1.75-2.25 for the former and 1.5-2.0 for the latter.

Of great concern to all sugar refiners is the sucrose loss to molasses. This is the percent of sucrose in the raws that will be carried to molasses by the non-sugars (ash and organic non-sugars (ONS) under ideal refining conditions. It is assumed that the ideal molasses analysis can be determined by the following formula:

$$Z = \frac{100(5 + 3g)}{3(3 + g)} = \text{Total Sugars}$$

where Z is the sum of the invert and sucrose in the molasses (as percent) and g is the invert to non-sugar ratio in the raw sugar. This formula is a modified version of the 1944 Tate & Lyle formula. It is assumed that the ratio of the non-sucrose constituents (invert, ash and ONS) in the ideal molasses and in the raw sugar are the same, and once the sum of the percent sucrose and the percent invert in the molasses are known, the rest of the analysis is determined by proportioning the various constituents, as shown below.

$$100 - Z = \text{Non-Sugars in molasses}$$

$$\frac{\text{Invert}_{(raw)}}{\text{NS}_{(raw)}} = \frac{\text{Invert}_{(molasses)}}{\text{NS}_{(molasses)}}$$

$$\text{Invert}_{(\text{molasses})} =$$

$$\frac{\text{Invert}_{(\text{raw})} \times \text{NS}_{(\text{molasses})}}{\text{NS}_{(\text{raw})}}$$

Z - Invert = Sucrose in molasses

$$\frac{\text{Ash}_{(\text{raw})}}{\text{NS}_{(\text{raw})}} = \frac{\text{Ash}_{(\text{molasses})}}{\text{NS}_{(\text{molasses})}}$$

$$\text{Ash}_{(\text{molasses})} =$$

$$\frac{\text{Ash}_{(\text{raw})} \times \text{NS}_{(\text{molasses})}}{\text{NS}_{(\text{raw})}}$$

Organic Non-Sugars in molasses =

100 - Z - Ash

Having determined an "expected" molasses analysis from a given raw sugar analysis, we are interested in the theoretical extraction values (sucrose to molasses and molasses %) and the Ideal Conversion which this raw sugar might yield.

The Ideal Conversion is the pounds of raw sugar that would be required to make 100 pounds of refined sugar if the pol. of the raw sugar were 96° and if the raw sugar were ideally refined with no resulting undetermined sucrose loss. The only refining loss considered here is the loss of sucrose to molasses. The sucrose to molasses loss is the percent of sucrose in the raws that will be carried to molasses by the non-sucrose (invert, ash, and organic non-sugars) in the raws under ideal refining conditions. This is calculated by the following formula:

Sucrose to Molasses =

$$\frac{\text{sucrose}_{(\text{molasses})} \times \text{NS}_{(\text{Raw})}}{\text{NS}_{(\text{Molasses})}}$$

The ideal sucrose loss to molasses is subtracted from the pol. to obtain the total sucrose per 100 pounds of raw that can be recovered by ideal refining.

To convert the raw sugar to equivalent 96° pol., a factor (Pol. -96. 0)x1. 4 is subtracted from the recoverable sucrose. The reciprocal of this difference is the Ideal Conversion.

Example:

Basis:	Raw Sugar Analysis:	Ideal Molasses Analysis:
Polarization	98.800	Sucrose: 45.39
% Invert	.282	Invert: 12.25
% Ash	.490	Ash: 26.49
% Moisture	.190	O.N.S. 12.87
% Organic non-sugars	.238	Sucrose to Molasses .840

Ideal Conversion: $98.8-.840-1.4(98.8-96.0) = 94.04 = \frac{1}{106.33}$

The expected Conversion includes an undetermined sucrose loss of 1. 0%:

Expected Conversion:

$98.8-.840-1.4(98.8-96.0)-1.0 = 93.04 = \frac{1}{107.48}$

To illustrate the effect of raw sugar quality on yield and molasses analysis, two raw sugars are compared in Table A.

Table A. Comparison of Raw Sugars

	1	2
Polarization	97.4	97.7
Invert	0.823	0.426
Ash	0.470	0.770
Moisture	0.857	0.221
Organic Non-Sugars	0.450	0.883
Non-Sugars	0.92	1.653
Invert to Ash Ratio	1.751	0.554
Organic to Ash Ratio	0.957	1.147
Safety Factor	0.33	0.096
pH	6.1	6.1
Color	130	230
Filterability	62	47
Crystal Size	34.9	23.6
Empirical Molasses Analysis & Yield		
G-Factor	0.894	0.257
Sucrose	35.13	48.524
Invert	30.63	10.547
Ash	17.49	19.066
ONS	16.75	21.863
Sucrose to Molasses	0.9439	1.960
Ideal Conversion	105.82	107.112
Expected Conversion	106.95	108.27
% Ash Removal	76.4	62.0

Sugar 2 has about the same pol. as No. 1 but about twice the Ash and Non-sugars -- when these calculations outlined above are carried through to expected conversion, Sugar 2 (a Peruvian Raw) sure enough requires significantly more raw to produce 100 lb. of refined than Sugar No. 1 (a Louisiana Raw).

To show how ideal and actual values compare, we have tabulated some recovery data over a 6 month's period (Table B).

This Table compares the actual measured values in the refinery with the ideal values calculated from the formulae presented previously. The difference was only 3.5 to 4.7% and indicates that the formula is indeed a useful guide. This table also allowed us to explain to management why a 10% increase in melt brought a 22% increase in sucrose loss to molasses.

Other variables in the raw sugar quality which we have found to affect refinery operation are:

Composition of Ash: With comparable ash levels, certain raws, notably Puerto Ricans, have a greater tendency to scale the heating surface of our white sugar pans than others. The scale increases our sediment level and boiling out of the pans reduces the melt. We have no yardstick in the form of an analysis at our disposal to accurately predict the effect of a given ash level.

Filterability Test: Since we do not polish Clarified Liquors, there is no correlation between this test and refinery performance. The amount of sediment in the raw as determined by the sediment pad gives us an indication of how much bagasse will have to be screened out in clarification. Excessive amounts mean additional labor and higher sugar losses.

Table B. Recovery Comparison
(6 Months)

		1967	1968	Change %
Daily Melt:		2,806,500	3,061,218	+ 9.1
Analysis: (Solids):	Pol.	98.272	97.987	- 0.29
	Inv.	0.785	0.868	+10.6
	Ash	0.395	0.486	+23.0
	ONS	0.547	0.656	+20.3
Affination Produced				
Lbs. Solids % Melt		8.193	10.015	+22.2
Gals. Per Ton Melt		20.13	24.61	+22.3
Molasses Solids Produced,	Actual	2.559	3.140	+22.7
	Ideal	2.365	2.793	+18.0
	Diff.	0.194	0.347	+ 4.7
Molasses Total Sugars,	Actual	1.771	2.148	+21.3
	Ideal	1.562	1.839	+17.7
	Diff.	0.209	0.309	+ 3.6
Molasses Sucrose (Clerget)	Actual	1.170	1.407	+20.3
	Ideal	0.805	1.001	+24.3
	Diff.	0.365	0.406	- 4.0

Crystal Size Distribution: We are faced with the possibility that most Louisiana mills will be using continuous centrifuges to purge high grade raw sugars in the next few years. We do not believe that the present method of evaluating grain size will be sufficient to evaluate the raw sugar from a standpoint of broken grain. The size distribution will become a more meaningful analysis.

In conclusion I would say that the following items are important: Percent ash removal in the wash plant, invert to ash, and organic non-sugars to ash ratio, loss of sucrose to molasses, percent molasses produced, yield as given by the amount of raw sugar required to produce 100 pounds of refined sugar, and ash composition and crystal size distribution.

E. J. Culp (American): I would like to add a few remarks to our panelists' presentation.

To provide a little background concerning the context in which we must work: raw sugar buying and selling is not simply a technical or scientific matter. It involves many scientific principles, as we have just heard. However, there are numerous facets of the business that are only remotely related to scientific factors, and I'd like to outline what a few of these are.

In the first place, the United States sugar industry cannot buy raw sugars selectively under the terms of the Sugar Act. This is the rule under which we work. The Sugar Act is the license that we have to stay in business. Now there are a few individual companies that are in a position to buy raw sugar selectively, but the industry cannot, and the larger members of the industry such as ourselves, must buy raw sugars that the U. S. Government says come within the definition of raw sugar as outlined in the Sugar Act. So, within this concept, we accept our responsibilities and say that we must be prepared to handle any raw sugar that comes along, provided that it is in a normal universe of raw sugars, i. e., provided that you could call it one of the main group of raws which does not have raw sugar quality characteristics way outside the normal range. Within this acceptance of responsibility, we feel that, if we are to have merit as refiners at all, and perform our job as it was intended, we should be prepared to accept hardships.

We should be prepared to accept problems, we should work hard when necessary. We should have extreme difficulty, when necessary, in getting raw sugars through our plants. If we wanted to paraphrase it, we'd say we have to grunt real hard and groan real hard and, yes, have tough problems, but this is our job. This is our job to refine sugar, even with difficulty.

However, there comes a point where you exceed the acceptable economic limits, and this is what we have attempted to collectively discuss here, -- where do we reach this limit? So we're attempting to set specifications, describe characteristics of quality that should be limited and talk about how the limits should be developed.

One other thing-a principle that we adhere to, and which, perhaps, other refiners don't agree to-we look at the principle of price adjustment according to polarization. We all know we buy raw sugars at a 96° price, and then there is an accepted formula that has been in existence for many years, that adjusts the price upward or downward according to polarization. Now, this is not an "equitable formula"; this is something that has been developed and exists by tradition. I am sure that with the adjustment from 96 to 97 degrees, one refinery may make a profit on that adjustment, while another refinery may lose money. It is inconceivable that an adjustment of that kind would apply "equitably" for all different refining processes. They just don't all work in the same way. But the industry has accepted, over a period of time, the general fairness of the adjustment.

Now, what do we do when we expect a 97° raw sugar, but a supplier gives us a 98° raw sugar? This is fine, it's high in test but what should we expect about the quality char-

acteristics of that raw, aside from polarization. Well, our philosophy is that, knowing how raw sugar is made, if you centrifuge a raw sugar or maybe even wash it a little bit to make the test higher, that you should expect that the other components of the raw sugar would go right along pretty much in proportion to the lack of polarization. In other words if you went from 97 to 98, you would expect to have correspondingly less invert and ash and organic and moisture, leaving the proportion about the same. So that is a little of the background on how we develop such a ratio of say, ash related to nonsucrose solids. It's on the basis that if you buy high-testing raw or low-testing raw you expect the nonsucrose components to float along accordingly.

One other thing that is a commercial policy-we must keep in mind that, regardless of how scientific people feel, these are all matters for negotiation between buyer and seller. It isn't a matter where scientists can impose their preferences. There are still going to be practical, commercial transactions developed between people who hold the purse strings.

There are also very important psychological factors with this whole problem. In the first place, I think we all agree that it is a good thing to apply what you often call the carrot-and-stick philosophy. That is, let a fellow burn his fingers a little bit if he does a poor job, and at the same time offer him a prospect of reward if he does an exceptionally good job. So that is what is behind this philosophy of premiums and penalties. There is a great quality range in which the manufacturer of raw sugar can rest comfortably and say, "Well, at least I make a normal product, so I'm not suffering a penalty."

Another psychological factor is the need to eliminate the unfair advantage that has existed in the past for a producer who has made a greatly inferior product. It just doesn't seem fair to the rest of the raw sugar producers, the great mass of them, to allow a few individual ones to sell their products at the same prices as others, even though they are not doing the work of making a good product that everybody else is. This is just a matter of inherent fairness.

Finally, we have to keep in mind, in this whole thing, the natural orientations of buyers and sellers. We've had many many discussions with raw sugar suppliers, and it's only natural that raw sugar suppliers don't like a system in which they run the risk of being penalized. At the same time, we as refiners don't like a system where we may get stuck with a raw sugar that really bogs our refineries down and costs us tremendous amounts of money, even though we paid the money for a good raw sugar. So what I'm saying here is that there are natural psychological factors involved in relations between buyer and seller that affect all of our orientations and we must try to be reasonably considerate of this point of view in talking with the different people involved.

Now there's a legal point of view. It is unfortunate that a system like this has to be set up, where all sellers of raw sugar, for example, may have to pay the money to have their products tested--at last count I believe it was about $80 per sample for the tests to be performed--that, even though their products are uniformly good, and never involve any penalties or premium. It seems unfair. And yet, from a legal point of view our lawyers tell us we can't discriminate because the fellow always gives us good products. We can't tell you you're exempt and you don't have to have these tests made, and therefore there is an element of unfairness here but it's a matter of legality where we must treat all suppliers alike.

Another point here - one reason that there are different points of view which could have been avoided if we could have collaborated earlier, is a peculiarity of U.S. law that we as buyers of raw sugar or as refiners are prevented from collaborating with each other and setting up rules by which we will buy raw sugar. So now we find that, after the fact, we're talking about it and we're

having trouble sometimes to rationalize our different points of view.

As far as science is concerned, we're first involved, each of us, in delineating those quality characteristics that we feel need to be identified, the really essential ones that have to be pinned down for any system of quality control on raw sugar. Of course in our case, we selected, as you know, the moisture and the ash content of the whole raw sugar and then the color, filtration rate, and grain size of the affined raw sugar. There are other points of view, but in any event, the scientific approach is to develop those items that are really essential. Different ones of us here have made contributions in that direction.

A scientific approach is also involved in the establishment of the critical quality limits. Now this is a big job in itself, and involves differences of opinion and matters of personal economic values. For example, let's take color. Just where is the limit where the pinch becomes so great that you say, "I can't stand it any more and I've got to have some financial relief." It's a scientific matter, to a great extent, to establish this point.

Then, there's this matter of rationalizing and establishing schedules and premiums and penalties. Here, you'll never make everybody happy, so somebody has to take the bull by the horns and go ahead and put down some numbers. This is what we did. This matter is negotiable between buyers and sellers. Some of you probably know that there've been many sessions between buyers and sellers on this matter, and there have been alterations made to the original system to change it, refine it, and make it into the more workable one we go by now.

Finally, then, there's the scientific matter of trying to be practical rather than to follow an ivory tower procedure. When we talk about science on a research level, this is one thing; when we talk about science from a practical, everyday, commercial point of view, that is another thing. A lot of tests which we would like to perform - like very much to perform - from a scientific point of view, on these raw sugars, are difficult to put across. In the first place, in many cases the techniques are really not worked out well enough to recommend them worldwide. Even more important, there is the matter of the cost of making the test, which might be needed only in a few instances. Finally there is availability of equipment and the technology, worldwide, to consider. Stop to think of the locations of raw sugar factories, some of them in jungle areas, some of them in the remote mountains where you almost have to get in by packmule. Where supplies are not very generously available, where technical personnel are rather few, it's difficult for us to visualize what kind of tests, what kind of performance, we could set up for a worldwide standard, realizing that those people, too, have to do the work that we will be doing in our more modern laboratories. So we always have to look for the compromise between what is practical, what is not; what is economical, or what is perfection. So these are just a few thoughts as to the general scientific contribution that has been made.

Now as to results, we should mention these for a moment. Our own experience has been a little different from that described by some of our other speakers. There has, in our experience, been a definite improvement in the overall quality of the raw sugar. I don't mean averages; the average raw sugar quality is about the same, and we were not seeking to have the average raw sugar quality any better. But there has been a definite lessening in the number of raw sugars that come in with such horrible color situations, or with such inferior affination qualities, or with such really difficult filtration qualities that we just can't get the melt through the refinery. The reason we got into this system was that there were too many instances of that kind over a period of years, and it was reaching a crescendo. Year after year it was becoming worse. During the two years that the No. 10 Contract has been in

effect I can say that this has improved, as far as we are concerned.

Let's talk just a minute about the filtration test. I grant you this is a controversial test, it is not perfect, we would like to have a better test. Unfortunately, too many of the people who have criticized the present filtration test have just said "Let's not have any," instead of coming along and saying "Here is a better one, won't you consider this instead of the other one," or "This is something that is being considered now to improve it." But as to the practical results now, coming back to that level, I can say that in the beginning, we were having horrible amounts of down time in our plants due to inferior filtration quality of raw sugars. The last time I looked at the figures, companywide, within our own bailiwick, we had paid out more money this year in premiums for good filtering raw sugars than we had received from the raw sugar sellers in the way of penalties. And I can say that of the five raw sugar characteristics, qualitywise, this is the only one in which we had paid out more money in premiums than we had received in penalties. So that we tend to look at the practical results that you achieve by the system, even with its imperfections. It could be better, it should be, it will be; nevertheless, whether we have gotten from one spot to another, which is improved, or we have not, our own impression is that things have taken a turn for the better.

Now, that concludes the remarks of your panelists and your moderator, and we would like to open the discussion for general questions.

R. S. Patterson (C&H): With regard to Bob Tuson's comment that they disregard filterability because they use clarifiers and go directly to char, and then do not polish filter after char: in our clarifier studies, we ran tests with the clarifier effluent, and we thought we were doing a reasonably good job on our clarifier and getting good clarity effluent, so we didn't anticipate difficulty with the pressure filtration. But, surprisingly enough, in our viewpoint, anyway, we got considerable difference in filterability of that effluent. So this probably is associated with the filterability of the raw sugar. At any rate, there was a considerable variation; for instance, at our refinery we had 13 filter presses on washed raw liquor, and according to our test results we could get occasions where we would have required the 13 presses on clarifier effluent.

W. R. Tuson: I'd like to clear up a possible misconception here. You are absolutely right that we do not filter between our clarifiers and bone char; however, we do polish filter after char. We do not experience in our operation any appreciable variation in flow-through char with various raws. The only time that I can recall where we did experience this was when our clarifier station had not been expanded and we had expanded the melt considerably, and we were pushing the clarifiers pretty hard, and did run into some problems of flow on char. Beyond the char, at the polishing operation we're down to something that's pretty pure, and we naturally do not expect to have any effect there, so that from our point of view, the filterability doesn't have any particular application. I do recognize, however, that from the variety of processes that others employ, it probably has a great deal of importance.

P. F. Meads (C&H): First, I would like to mention what the Hawaiian sugar industry has done in this area of raw sugar quality and, second, to comment specifically on some of the No. 10 contract methods. The Hawaiian sugar industry has been concerned about sugar quality for many years. In fact, I have a report issued in 1917 that points out differences in the quality of raw sugars, and the fact that these sugars of different quality incur different refining expenses. In 1956, we became very serious about this, and actually looked carefully at the dollars involved. Now, we should all realize that the Hawaiian industry is in a unique position: there is no reason why we should optimize refinery results at the expense of the raw sugar factory, or vice-versa. We are looking for an overall economic benefit. This doesn't happen

in very many other places. We worked out a program with three aspects. One is a research program, to improve the quality of raw sugar. This is being carried on both at the Experiment Station in Honolulu and in our Crockett laboratory. The second part is an allowance program and the third is an interchange between personnel at the raw factory, the Experiment Station, and at Crockett. This interchange helps us to become better acquainted with one another's problems and to gain mutual understanding.

The allowance program was first started in 1959. We employed five quality factors: polarization, ash content, crystal color, filterability, and grain size. There were reasons for these choices which applied to a specific refinery, the Crockett Refinery. At that time, the Crockett Refinery had insufficient capacity at the remelt station; therefore, a floor on polarization was necessary. We were having some trouble with ash in the refined products, so a maximum ash restriction seemed reasonable. After we increased the capacity of our remelt station, we dropped the polarization from the allowance scheme. Ash was dropped because improvements both at the refinery and at the raw sugar factories eliminated it as a problem. The remaining three quality factors were, then: filterability, grain size, and crystal color. Initially we were dealing with methods that were not appropriate. For example, we used the Eliott filterability test which filters a solution of whole raw sugar. Well, we don't filter whole raw sugar in the refinery. We were using a very tedious, difficult and poorly reproducible wet screening method for grain size. In color, we were dealing with obsolete units, the Stammer degree. One of our first requirements was to develop new methods. These were presented by C. W. Beal at the S. I. T. meeting in 1963. These new methods were developed collaborative by Crockett and the H. S. P. A. Experiment Station. We have found these methods to be reproducible and generally satisfactory. Initially we tried to obtain a standardized affined sugar. We gave that up because we could not obtain satisfactory standarization. So we went to complete washing of the crystal -- getting rid of all film. If you look at the washed crystals in our laboratory test under a microscope, you see very sharp crystals but no film. These washed crystals are used in our new color, filterability, and grain size tests.

We are not compelled to stand with these three factors for evermore. This is a developing program: as we have already dropped a couple of factors, we may add some others in the future. We know, for example, we are overlooking the qualitative aspect of color. Some colorants are more easily adsorbed than others. We are going to see if a simple test can be devised to measure ease of decolorization. It is possible that other properties, more closely related to refinability, can be measured and can then be included in the program. This program does work, and has benefited both the refinery and the raw sugar factories.

Now, to get back to the No. 10 contract methods, I want to mention one or two things which bother me. I've already covered the affination problem. On the color method, I would like very much to see readings at the 420 nm wavelength rather than at 560 nm. I mention this as ICUMSA referee in this area. We are trying to standardize color methods and reduce the number of methods now in existence. The overwhelming tendency is to use 420 nm. We've heard some of the problems with the filterability procedure. We sell some of the Hawaiian crop under the No. 10 contract provisions. We make tests by the No. 10 contract methods. And we find that there's a marked difference in the reproducibility of the No. 10 contract method and of our own internal methods. We are surprised, sometimes, at the variation we get between the three laboratories on the No. 10 contract method. Our method is much more reproducible. Why don't we make this available? Well it is available, and for the people who are visiting Crockett in the next day or two, we're set up to demonstrate it.

E. J. Culp: I would like to ask you a question about this 420 vs. 560. If we were to switch over and adopt the 420, could you give me any assurance that we would never find any reversals, in other words, that we would always find the 420 reading to be pretty much in accordance with the 560, i. e., we would never have a raw sugar manufacturer challenge us because we said it was a dark colored raw sugar where he could point out and hold it in front of us and say "See, it's really good after all." Are we really protected if we switch over to 420?

P. F. Meads: I think that whatever you use, you're using something that's arbitrary. Your 560 nm. is arbitrary. I know the argument is used that the human eye is most sensitive in the green but remember the spectral curve of sugar solution. There is less adsorption in the green than in the blue. In looking at a sugar solution, the maximum response depends on both the spectral sensitivity of the eye and the spectral curve of the sugar solution. Blue provides a better response than green. Moreover the trend, throughout the world in the sugar industry is to move toward 420 nm. The spectral curves of sugar solutions are not all parallel. If you were to take a number of these curves, you would get slightly different ratios between the values at 420 and 560 nm. However, there is no reason to prefer the 560 nm. reading to the 420 nm. reading. Either one is taken as the point to read color purely as a matter of definition.

F. G. Carpenter (SRRL): While we're on that subject, through the years I have made quite a few measurements at 560 nm, at 420 nm, and also by visual inspection. Our reports (1) show that 420 more often agrees with the visual appearance than 560 does.

F. M. Chapman (SuCrest): I have been wondering about our philosophy of purchasing raw sugar, and in particular about our standards. Would any of us accept the standards of 5, 10, or 20 years ago if we were buying tires or automobiles or bone char or paper bags? In short, our customers expect more of us, so we should in turn try to improve our raw sugar. We have a duty to our organizations to reduce the processing costs. In the United States, the United Kingdom, and Canada, there is a fair amount of work being done in refineries that might be done in the tropics at much less cost. We don't need to be any deeper in the garbage business than we have to be. We all know that the essential job of a refinery is to do the final biological laundering and produce an assortment of products as and when required. A fairly good approach to many problems is to ask what one would do to idealize a situation. So, if we idealize a raw sugar, what would we ask for? It would be low in ash, low in organic matter, low in color, low in moisture, and low in suspended matter. We have had today some very interesting papers about color, on which we make great efforts, and spend much money to remove. Are we doing nearly enough about not making color? I have recently been digging through my papers, and have observed a very marked dependence between color and invert and temperature. In general, apart from recrystallization, there is not much we can do about invert, but there is certainly a lot we can do about temperature.

J. F. Dowling (Refined Syrups): One of the main things that concern me most about these new raw sugar evaluation methods was their precision. We like to have our analysis included in the final evaluation determined by the results reported from these three different laboratories at least 70% of the time.

We initially found that we were eliminated 50% of the time on color, and were consistently high. In reviewing the method with Dr. Binkley, I found that the filter aid we were using was making a big difference. At the present time we are using three different types of filter aids, supposedly all standard brands, and arriving at three different colors. One type of filter aid has consistently given us a high color which I would attribute as

(1) Deitz, V. R., J. Res. N. B. S. 57, 159 (1956), Bone Char Tech. Reports No. 32 and 34.

being partly due to turbidity since this brand always gives high absorbance at 720. To better standardize this test, I feel the color should be determined by using two wavelengths and 720 should be one.

We have also noticed that during the washing of the various raws, some wet more easily than others and a more uniform magma is obtained. The new revised procedure increased the melted granulated used in the washing from 342 to 380 ml. and this has helped, but I still feel that a larger amount can be used. It is better to wash with an excess and be sure all the affination is removed. In the past we have found better reproducibility when using an excess of melted granulated in washing the raw.

The second method which we had difficulty with was grain size. We found that we got better reproducibility by washing the raw sugar directly with the methanol rather than the washed raw sample. It is very difficult to uniformly wash a raw sugar in the laboratory, and I feel the largest errors are in the affining and washing of the raw sugar. By directly washing the raw with the alcohol, these errors would be eliminated.

Since we have been performing these tests there has been some improvement in the raw sugar quality. I think the raw producer who is faced with a large penalty has made a greater effort to meet the standards. My company, like many others, would prefer to see the ash determined on the washed raw sugar. At this time I think it is up to the refiners who prefer this to say so. I don't know if my company will incorporate this in our contract this year, but I think we all owe American Sugar many thanks for developing these initial standards.

A. J. Clarno (Savannah): I would compliment anyone who would make an effort to set up standards for raw sugar. However, I have wondered why color standards were set up on affined raw sugars rather than on whole raws. The affination has to be faced up to sooner or later anyway. The colors in the syrup film must be eliminated by refining.

E. J. Culp: This is an excellent question and it ties in with some other questions on ash. It has to do with this idea. What do you expect when you get a lower testing or a higher testing raw sugar? Some place along the line you'd have to say, other things being equal, that you expect "so and so". And our philosophy is, that in general, a higher testing or a lower testing raw sugar, by and large, indicates more or less syrup film on the crystal. Once you accept that theory - which is one way of looking at it - that a lower testing raw sugar has more mother liquor or more molasses film on the crystal, then you are around to the point where the affination process can be expected to produce the same quality of washed raw sugar, regardless of the test. In other words, suppose you could get raw sugar as high as 99.9 polarization. If you were still following the same process of mingling with dark, dirty-colored affination syrup, the chances are you wouldn't have so good a washed, raw sugar. So this is the point of view on which the test was based. It is also tied in with the fact that many years ago refiners used to char filter all of their affination syrup. I don't think anybody does this today; at least, it's rare if it's done anywhere. Most people today take the affination syrup and push it off as fast as possible through the remelt system and into the blackstrap. So even though you are partially right (some of the color does come back in the remelt or recovery sugars) a great deal of this color that's in the affination syrup never sees the refining system, because it goes out in the blackstrap. So it's a matter that isn't clearly black or white, but somebody has to take a scalpel, so to speak, and cut down in a certain direction. This is what we did with the problem.

P. F. Meads: Following up on Mr. Clarno's remarks, I think that probably one of the next additions to our quality factors would be whole color, because certainly the portion of the film that's left on after the affination step gives a lot of problems. Then, following that, we would hope to have an "ease-of-decolorization" test. Maybe somewhere we can combine these and our crystal color to give both

a quantitative and a qualitative aspect to color.

I was interested in Mr. Dowling's comments about the way in which he had changed the ratio of syrup to sugar. This again points to the problems with a laboratory affination step. He has done this, apparently, to take care of certain sugars. However, in so doing, he has upset the standardized procedure. Now, in some sugars he is overwashing. So here we have another example of the difficulty of relying on a laboratory affination step. I think that this is one of the really critical problems.

H. G. Gerstner, (Colonial USA): Has anyone given any thought to the relationship between Pol and Clerget? It is very discouraging to get a cargo of sugar in which the polarization is higher than the Clerget.

E. J. Culp: I am sure that the inventor of a better test than polarization will reap great rewards if he patents it and distributes it properly.

P. Petri (Godchaux-Henderson): Mr. Gerstner's remark, concerning the discrepancy between the Pol and Clerget: we feel that you should make a determination of the dextrose/levulose ratio on the raw sugars. It happened last year in Louisiana, where the farmers had an exceptionally good crop, that at the end they got a little greedy and stopped topping the cane. We found that the dextrose/levulose ratio got out of hand and we got into trouble because we didn't exactly know what the basis for payment was, and we probably paid more than we should have. So we think that this determination is something that should be done.

C. W. Davis (Colonial, Australia): I would like to take you back to meet a cane physiologist who said to me, "What sort of cane should I be making?" And I said "Just cane with sugar in it, that's all." He said "Yes, but I have to put something else in it. What else don't you want in it? What else will you accept in it? Give me some tests with numbers that I can apply." Now this is not a romance. This actually happened to me. We have a physiologist who would rank with any physiologist in the world, and he has a team who are willing and anxious to go, but we can't tell him what we want. This is problem number one. Problem number two--we come to the people who harvest and deliver the cane and find a similar situation. We say, "Oh, we don't like the way you harvest the cane--there is too much rubbish with it, or it lies too long in the field." They say, "Well, just give me some measures--some working rules." We come to the factory and we find a very similar set of circumstances. Now this is not news to you all, but I am trying to emphasize that throughout this industry we are relying very much upon expert opinion. The expert opinion is not enough, because we know--those of us who really think about it deeply--that we cannot really write a prescription for the sugar we want.

To get ahead of myself for a moment--my view is that there is a very healthy state of affairs existing at the moment in that we are having so many of these forums. I think that since we have established a practice of discussing and emphasizing these basic problems, and are now actually doing something concrete about them, some remarkable changes are occurring.

If you look at raw sugar milling, you will find a gentleman sitting with his hand on the cashbox saying "You can't have another vacuum pan." You must therefore find out what will cause him to give you another vacuum pan or any other piece of equipment, for that matter. It won't be his own employees--the people in the sugar field who are quite remote from the markets of the world. There is always this perpetual struggle for the balance. At the ideal balance, the refiner and miller are optimizing their total capital investment.

I am overjoyed to see the work that is going on, particularly on color. It is a beginning, and for the first time in my life I feel that we are beginning to see the real

nature of quality problems. Fundamental investigations of this nature are, I believe, greatly aided by large group meetings such as this one, where research scientists and production men can stimulate one another by an exchange of ideas on basic problems. We must guard against complacency, and we cannot allow the acceptance of an arbitrary set of rules and numbers, which work fairly well, to prevent further work on fundamental problems.

To return to the problem of color: I feel that we have barely begun, but have made a constructive start. We must now endeavor to survey all aspects of the field, determine the few lines of research that should prove most fruitful, and then make sure that high level talent is put to work along these lines. We must have organic chemists working for us, in addition to non-scientist sugar men. We have already made progress, just in the past two years, in convincing scientists of the importance of our research. This must continue and increase. We must now push for supporting work from universities and research institutions, and it is our responsibility to ensure that the lack of financial backing is not a deterrent to further research. To give an encouraging example: ISSCT has declared that, out of all possible areas they could work in as a body throughout the world, the ISSCT will officially back fundamental research work on crystal inclusions.

There are, at this time, one or two university projects on inclusions: we must attempt to quadruple this number, and initiate work on inclusions in crystals growing at industrial rates, not near equilibrium, in high viscosity media. We must also increase research on the mechanism of growth of the raw sugar crystal. One of our men is doing a doctoral thesis on this in the University at Queensland, and the chemical engineering school in that University has chosen to take a continuing interest in this area. ISSCT has chosen crystal shape and size as its other fundamental area of support. It is heartening to see research at last directed along specific lines! After all, if you back every horse in the race, you don't win much money.

Now, about grist: I should like to know if there is anyone here, or anyone you know of, who can relate some measures on the raw sugar quantitatively to its affining quality? Can you put some tests on a raw sugar and from those tests evaluate its relative worth in the affining station? One of the projects that will, hopefully, be launched soon, is the design of a way to evaluate various sugars as to their grist. This implies fugal trials, presumably affination trials, not only data on how a sugar will behave in existing fugals, but perhaps suggestions for new ways of affination--perhaps a fluid bed method. There is still plenty of scope for evaluating grist in raws and deciding how the relative amounts should influence the making of sugars of certain types--and also the washing of raws.

Well, we evaluate them, and then we say "Now, what about designing vacuum pans with these factors in mind?" The vacuum pan designer says "Oh, yes, I want to get less fines in the sugar." Then he says to the refiner, "If I get less fines, what will you do for me?" But the refiner says, "Oh, I'll give you a vote of thanks." Now you know how much use a vote of thanks is--you don't want a vote of thanks--you want to be convinced that your design is worthy, and the pan designer does not know the value of changing the grist of the sugar. So then we get back to pan design and we find that we don't even know how to measure the grist of sugar without a lot of pain.

It seems to me, then, that we have a lot of work to do in formulating what problems there are, and with what conviction we can get others to commit themselves to these problems. This is a rather general expression of my convictions; I find people get resentful when I point out these needs, because they constitute a very hard thing to do. However, I think that in the color area we are doing this.

My main reason for speaking, really, it to say that I think our main need is to keep forums such as this open, and while, for reasons of expediency, we have to settle on

various forms of quality, we must not lose sight of our basic goals. We must keep these forums open, and make sure that we are also conscious of other organizations, such as ISSCT and ICUMSA, that can be of help.

E. J. Culp: Thank you very much, Mr. Davis, your thoughts are thought provoking and inspiring, and they give us a lot to think about.

W. L. Reed (Revere): We, at Revere, do not have a large research facility, so one of the things that we have to try and do is to start with what is necessary and perhaps, by making a small change or addition, obtain much more data at a minimum of extra work. As we have to read a specially filtered solution at 560 wavelength we automatically read at 420 anyway, because we have the solution. I would like to put in a vote for 420 as a basic reference wavelength. This way you automatically have the Q value, which can give you some idea of the type of color of the raw sugar. One might even use the 520 and 455 wavelengths that were proposed this morning.

On grain size, we tried screening the raw sugar itself and found that we could work out a very acceptable raw sugar screening on the cargo, which correlated very well with the screening of the centrifugal washed sugar. So, it is possible to check a series of portions of a given cargo (if you happen to have a 40,000,000-lb. cargo with a wide variety of sugars), or any other samples without the trouble of running the separation in the laboratory.

Also. since you have to prepare the sample anyway, and that step is the biggest amount of work, we do the complete screening in addition to the "through 28" fraction and thus get the MA and CV as an extra crystal evaluation.

On filterability, although we haven't been able to do too much, we have found that there's possibly some significance in the filterability of the 15 Brix solution of the "whole raw"--merely screen out the junk through a 325 mesh screen first. It is surprising that for some of the washed sugar filterabilities which have varied from 35 to 150 (in the few cargos we've studied) the whole raws have run from 10-75 under identical conditions--possibly the ratio or the differential between the raw and the crystal filterabilities might have some significance.

I'd also like to put in one more vote for ash determination in the centrifugal raw sugar as we've been doing that since the start and feel it's very important. In one year, we've had cargos .07% to .25% ash in the crystal, and when you're concerned with your first run char liquors to some degree that is significant.

Lastly, I'd like to ask if anyone has a method for making a "reference wash syrup", (corresponding to the "washed sugar sample" we now get). I would be interested to hear of it either by mail, or in the proceedings.

James C. P. Chen (Peru, by correspondence): As technical representative of the Peruvian Sugar Industry, and a participant at the technical sessions held in New York in 1966 and 1967 between buyers and sellers, I fully agree with C. W. Davis: to keep forums open can be of help to both the refiners and the producers. By providing more data and information from the researchers and scientists of both refiners and raw sugar producers, the "Raw Sugar Quality" could be less arbitrary and more applicable to different systems of refining operation.

The refiners may specify whatever standards suit their purposes, but for raw sugar producers, it is not so easy to prescribe standards and to conform to them.

We, the raw sugar producers in Peru, feel that the "yardsticks" such as pol, moisture (expressed in safety factor), grain size, filterability and color are good indications which are somewhat correlated to the refining operations. But not, however, the specification of ash, as expressed in ratio to the total non-sugar solids.

Since the No. 10 Contract was put to work in 1967, much attention has been paid to the methods of analysis and little has been done about revision of the specifications. For instance, during this meeting, someone brought out the determination of color with 420 nm. instead of 560 nm. This is a better specification, because it is more significant and may be more correlated to the refining operation. Someone also voted for ash of washed raw rather than Ash/NSS in total raw. The ash is a "yardstick" that must be investigated.

Although the levels of Penalty and Premium have been lifted a little bit in 1968, their meaning is more commercial than technical.

Talking on ash as my specialty, the Ash/NSS only shows one side of the story. The other side should be the quantity of ash. We all know that the loss of pol in blackstrap is not only expressed by the blackstrap purity, although the purity of blackstrap is liberally used as a good indicator. When I say not only, I mean that there is another factor to be considered. Let us use simple mathematics:

100 ton. Blackstrap x 50% Pol = 50 Ton. Pol loss.
75 ton. Blackstrap x 60% Pol = 45 Ton. Pol loss.

↑ less ash (in quantity) gives less melassigenic effect and so could give less quantity of molasses.

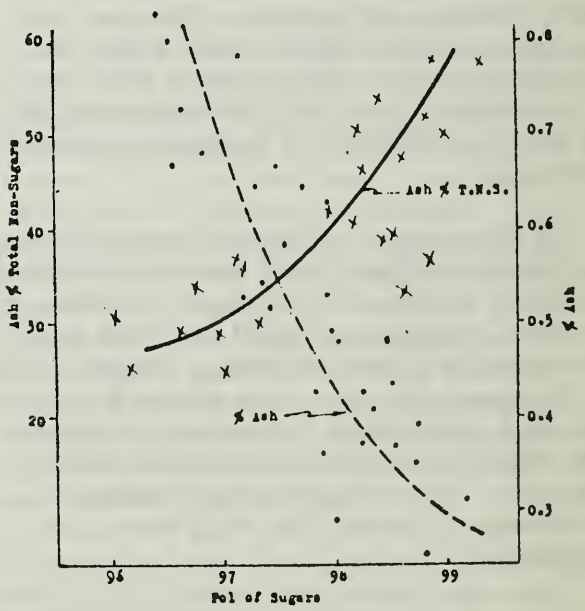
↖ higher ash/N. S. S. may give higher blackstrap purity and so higher pol.

Reports of former researchers could evidently support the quantity of ash in relation to loss of sugar to the final molasses. (Honig's Principles of Sugar Technology, Vol. III, 513, 539, etc.). So what I would like to point out is that higher purity does not necessarily mean a higher loss of sugar in blackstrap.

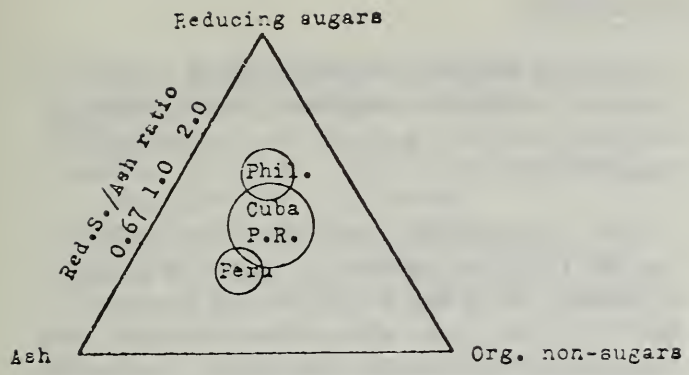
In theory and in practice, the quantity of ash should have its role in a refinery. The ash increases the solubility of sucrose and so, the more the quantity of ash, the more loss of sucrose to blackstrap. The ash also increases the formation of scale in evaporators or pans, which is related to the quantity of ash rather than the ratio of Ash/NSS, as already pointed out by W. R. Tuson.

Let us use the example of Peruvian raws. Due to 100% irrigation and long growing season, the sugarcane naturally contains higher ash, but lower invert, resulting in a higher ratio of Ash/NSS. To expect the changing of this ratio, at least in Peru, would seem to be as easy as to make a Chinese become Caucasian.

Mr. Culp expects that by increasing the pol from 97 to 98, the proportion of Ash to NSS could remain the same, but it is not so in Peru, as could be seen from the following curve, and figure. (Chen, J. C. P., Proc. S. I. T. (1967).



Ash % N. S. S. and Total Ash of Peruvian Raws



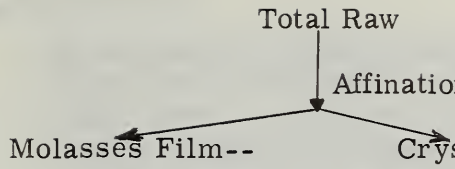
Composition of Raw from different countries

The raw sugar producers, with the conventional defecation process, could not change very much in the ratio of Ash/NSS, but could do something to reduce the ash quantitatively.

For some refiners, the emphasis has been on a total ash of less than 0.5%. To attain this limit, the raw producers have a method: either the total ash or the ash in grain, or both, could be changed. But in changing the ratio of Ash/NSS, the lower quantity of ash might show a higher Ash/NSS, as could be seen from the examples. By increasing Pol in order to reduce the Ash content, the lower Pol is free of penalty while the higher Pol, with less Ash, suffers the penalty.

Pol	97.00	98.84
Moist.	0.62	0.27
Ash	0.70	0.36
Red. S.	0.57	0.41
Max. Ash	0.76	0.32
Penalty	Free	4 points

Actually, what happens to the ash in a refinery could be shown in the different operations, thus:



Ash in film affects recovery (Ash in quantity as well as in ratio with NSS)

Ash in crystal, or specific ash constituents, affect decolorization and increase the scale formation in pans. (Ash or ash constituents in quantity seem to have better correlation).

As to the penalty and premium, the refiners apply a so-called carrot-and-stick philosophy which, as explained by a commercial executive, is a 1 point encouragement to 2 points discouragement (penalty). The raw sugar producers are only able to try to reduce the possible penalties. The plan does not show the desire of the buyers to obtain better raws -- as pointed out by Frank Chapman.

The raw sugar producers strongly feel the necessity to build a better relationship between buyers and sellers so that both sides, as mentioned by P. F. Meads, may become more acquainted with one another's problems, and gain some mutual understanding.

CLOSING OF THE SESSION

E. J. Culp: So we have come to the time to close our meeting. In doing so, we have a number of things to reflect on. We've had many interesting papers and discussions. We all have a great deal of thanks to express to Dr. Carpenter for arranging this program. He certainly did a splendid job. On the other hand we are conscious of the fact that he did not act alone. We are specially grateful, in addition, to C&H for playing the part of hosts at this meeting, providing such fine hospitality as well as assistance in arranging the meeting, and thanks go specially, in this regard, to Dr. N. H. Smith, for the local arrangements that were made. We all realize what a fine job Phil Meads did last night as MC at the banquet. We also must especially thank Mrs. Arlene Gil and Mrs. Elsie Roberts, who not only functioned efficiently behind the desk, but also were most pleasant to talk with and to see at each of our sessions. I think this covers the most prominent workers in this program and the arrangements. There are many others, of course, behind the scenes, who functioned, and I hope any omissions will be forgiven because we give thanks to anybody who contributed in any way.

Our next meeting will be October 5 and 6, 1970, in Boston, so that will be quite a switch, from San Francisco to Boston. We'll try the other side of the continent, perhaps some Boston baked beans and some lobster will taste just as good as the fine foods we had out here. In conclusion, let me say that we all have a lot to look forward to. We've all been inspired, I'm sure by the work on color today that represents the recent activities of the project at New Orleans. We have all been inspired, too, to hear Dr. Farber talk and also to learn of Miss Clarke, the new addition to Dr. Carpenter's team. With this trio of three doctors, three people who are not only competent, but who are also inspired in their work, we can certainly look forward to big things during the year to come. So if there's no further business, we'd like to wish everybody a most enjoyable further stay in San Francisco and a safe journey home.

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